Determination of Nitrogen Concentration in Dilute GaNAs by STEM HAADF Z-Contrast Imaging

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Abstract. We determine the nitrogen concentration of Ga\textsubscript{N\textsubscript{0.01\textless x\textless 0.05}}\textsubscript{A\textsubscript{1-x}} quantum wells by evaluation of high resolution scanning transmission electron microscopy (STEM) images using a high-angle annular dark field detector. Although nitrogen has a smaller atomic number than Ga the image intensity increases with the nitrogen content. This is explained by the influence of static atomic displacements by comparison with frozen lattice simulations. The resulting nitrogen concentrations agree with high resolution X-ray diffraction measurements and strain state analysis applied to STEM images.

1. Introduction

As small amounts of nitrogen reduce band gaps of ternary GaNAs and quaternary InGaNAs, these semiconductors find many applications in the fields of electronics and optoelectronics. The large bowing parameters allow tuning over a wide spectral range by setting the nitrogen content. For all those applications an accurate understanding of the structural and chemical morphology is important. For investigation of dilute semiconductors high-precision techniques are essential. In this proceeding we employ high resolution (HR) scanning transmission electron microscopy (STEM) imaging of GaNAs/GaAs using a high-angle annular dark field detector. The HAADF intensity mainly stems from thermal diffuse scattered electrons, thus depending on the atomic number of the scattering atoms \cite{1}. In STEM images intensity maxima of the HR pattern can directly be used to measure positions of atom columns, which is an advantage over conventional transmission electron microscopy (TEM) where positions of extremal image intensity depend on imaging parameters, lens aberrations and gradients of specimen thickness and composition. We show that the correct interpretation of STEM intensity requires to take into account the influence of static atomic displacements (SADs) that occur due to the small covalent radius of nitrogen atoms compared with gallium or arsenic \cite{2, 3}.

2. Experimental Procedures

The sphalerite type GaNAs/GaAs sample was grown by metal-organic vapor phase epitaxy. Five Ga\textsubscript{N\textsubscript{x}}\textsubscript{A\textsubscript{1-x}} quantum wells (QWs) with varying nitrogen concentrations \textit{x} between 1 and 5 percent were embedded in GaAs. The nominal values of nitrogen concentration were derived
from high-resolution X-ray diffraction (HRXRD) measurements. The QWs are separated by 80 nm spacers and have a width of approximately 10 nm. We prepared an about 160 nm thick TEM lamella by focussed ion beam thinning using an FEI dual beam system Nova Nanolab 200. Final thinning step was performed by ion milling at 400 V using a Technoorg Linda Gentle Mill IV5. All STEM measurements were performed with an FEI Titan 80/300 microscope operated at 300 kV. The specimens were viewed along the [001] direction. We used a camera length of 196 mm where the Fischione 3000 HAADF detector covers an angular range between 33 mrad and 200 mrad. Imaging conditions were chosen as suggested in [4]. These conditions avoid saturation of the detector and provide a linear signal transfer of the amplifier. We scanned 2048 × 2048 image points with a dwell time of 16 µs, the scan direction was chosen parallel to the growth direction to minimize the influence of specimen drift on the measurement of atom column positions.

3. Simulation of Reference Data

STEM reference data were computed with the STEMsim program [5] using the frozen-lattice multislice approach with supercells of 9 × 9 unit cells size perpendicular to the electron beam direction. Each unit cell was scanned with a resolution of 20 × 20 picture elements (pixels). The convergence angle of the electron beam was set to 9 mrad, the spherical aberration constant of the condensor lens was defined to be 1.2 mm. Images were simulated for supercells with nitrogen concentrations between 0 and 8 % in steps of 2 %. Intermediate concentrations and thicknesses were interpolated by polynomial fitting. We implemented SADs by relaxation of the supercells using a valence force field model [2, 6]. Debye Waller temperature factors were taken from Ref. [7]. The non-homogeneous sensitivity of our HAADF detector was taken into account. To suppress biasing of measured concentrations towards higher values in regions with a concentration of zero due to noise, the reference data set was extrapolated towards negative nitrogen concentrations.

4. Evaluation of nitrogen concentrations

For determining the nitrogen concentration within a GaNAs QW the QW itself as well as part of the GaAs region was imaged. In a first step the positions of the atom columns are found. For this the original STEM image was Wiener filtered and short-range fluctuations were reduced by applying a low-pass filter in Fourier space. All further steps are performed with the original unfiltered image. Next, the image area is segmented into Wigner-Seitz cells. Then the image intensity is averaged within each cell which gives the local mean intensity. From the HAADF intensity of the pure GaAs we deduce the specimen thickness which is extrapolated to the nitrogen containing region by a polynomial. For doing this the ratio of HAADF intensity to incident electron beam intensity is to be measured. Latter one was determined by a detector scan. With known specimen thickness the HAADF intensity in the QW region is then directly associated to a specific nitrogen concentration given by the simulated reference data.

5. Results and Discussion

The approach is described exemplarily on the basis of an HAADF STEM image containing a QW with a nominal nitrogen concentration of 3.3 % at a magnification of 3.6 Mx. The applied magnification was chosen to achieve adequate high resolution (the pixel size is about 50 pm) on the one hand and a large GaAs reference region on the other hand. Latter one is important because the regions next to the QW show decreased intensity and can therefore not be used as reference signal. This effect is due to surface strain relaxation [8] and depends highly on the amount of nitrogen in the well. The mean thickness obtained from the STEM image was 165 nm.

Figure 1 a) shows an HAADF image of all five QWs of the investigated specimen. Considering only scattering depending on atomic number, one would expect an inverse contrast ratio: the
imaged GaAs should be brighter compared to the nitrogen containing QW (e.g. observed by Herrera et al. [9]). However, taking SADs into account, we observe a different behavior: for typical STEM specimen thicknesses above 50 nm, the HAADF signal increases with nitrogen concentration. Figure 1 b) shows the simulated HAADF intensity normalized to GaAs for selected concentrations.

Evaluation of the nitrogen concentration as described in section 4 yielded the concentration map depicted in Figure 2 a). Averaging the concentration values along atomic rows parallel to the QW gives the concentration profile shown in Figure 2 b). The errorbars involve the standard deviation caused by intensity fluctuations as well as actual concentration deviations divided by the root of the number of positions that account for the calculated mean value (standard error).

We find that the nitrogen distribution is well confined to the QW area with rather sharp edges. The regions next to the QW cannot easily be evaluated because surface strain fields influence the HAADF contrast and the concentrations in these areas do not belong to real nitrogen contents. For defining the mean concentration value from Figure 2 we trust the values close to the center of the QW because there surface strain can be neglected due to symmetry. Here we find a nitrogen concentration of 2.8 ± 0.6 % which agrees with the nominal value of 3.3 %. This effect was well reproduced in simulated images where elastic relaxation and lattice plane bending were taken into account. These results will be published elsewhere.

Figure 3 a) shows the N concentrations derived from HAADF intensity evaluation for all five QWs. We measured at four different positions on the specimen for each QW. Shown are the mean values of these positions, the errorbars involve the standard deviation only. Taking the errorbars of each single measurement into account the accuracy of the concentration determination is about 1 % N. To obtain further values for comparison we evaluated the same images in terms of a strain
state analysis (SSA). The nitrogen in the QW leads to a smaller lattice distance compared with GaAs reference regions. From the image we determine the tetragonal distortion for each position of the atomic columns from which the nitrogen concentrations are calculated applying Vegard’s law and assuming complete tetragonal distortion (thick specimen limit). The concentrations derived from SSA are shown in Figure 3 b) where the values are presented in the same way as in Figure 3 a). Concentration from SSA agree with those from intensity evaluation and with nominal values when taking single measurement accuracy into account. So a combination of SSA and HAADF intensity evaluation provides a concentration determination with enhanced reliability.

6. Conclusion
By taking static atomic displacements into account, the comparison of STEM HAADF images of dilute GaNAs quantum wells with simulated reference data allows a nitrogen concentration determination with an accuracy of 1 % N. We verified our results by evaluating the same images with strain state analysis.

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Figure 3. Concentrations measured for all five QWs a) by evaluation of HAADF intensity and b) from strain state analysis. Shown are the mean values of four evaluated areas in each case. The errorbars represent the standard deviations and do not contain the error of the single measurement.