

## Nanoanalytical quantification of the nitrogen content in Ga(NAs)/GaAs by using transmission electron microscopy in combination with refined structure factor calculation

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We have studied systematically the nitrogen content in Ga(NAs)/GaAs quantum wells by (002) dark-field transmission electron microscopy (TEM). The nitrogen contents derived from this analysis, when assuming that all the atoms occupy their unperturbed positions in a virtual crystal, deviate significantly from the nitrogen contents we derive for the same samples by other methods; for example, high-resolution x-ray diffraction (XRD) and dynamical simulation of those XRD patterns. The nitrogen causes a significant local strain in the crystal and can accordingly displace the neighboring atoms dramatically. We show that, if the structure factor of the crystals is recalculated, taking these static displacements of the Ga atoms into account, the composition derived from the TEM analysis with that from XRD is in perfect agreement. It is hence necessary for tetragonally distorted crystals that have mixed sublattices containing atoms with different covalent radii to take these static displacements into account when quantification of the composition from dark-field or high-resolution TEM images is aimed for. © 2006 American Institute of Physics.

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The dilute N-containing ternary and quaternary alloys Ga(NAs) and (GaIn)(NAs) are of considerable technological interest as the N induces a theoretically predicted<sup>1</sup> and experimentally proven<sup>2</sup> strong bowing of the band gap in these materials and hence allows for emission wavelengths in the range of 1.3 to 1.55  $\mu\text{m}$  on GaAs substrates. Since the composition of the quantum wells (QWs) as well as compositional fluctuations within quantum wells and the interface morphology of the quantum wells with the barrier material influence optical and electrical properties, nanoanalytical characterization of these materials is indispensable. For this purpose, transmission electron microscopy (TEM) is frequently used as it opens up the possibility to determine the composition of these materials on a nanometer scale. To quantify the composition of mixed III/V semiconductors having zinc blende structure dark-field (DF) imaging with the weak but chemically sensitive 002 reflections is frequently used. The experimentally observed image intensities have to be compared to Bloch wave calculations,<sup>3</sup> which are based on the precise knowledge of the structure factors of the crystals under investigation. Structure factors are influenced by atomic scattering factors as well as the atomic arrangement in the unit cell.

The incorporation of nitrogen atoms in Ga(NAs) causes local strain fields that affect spatial positions of the neighboring atoms. Such a strain field causes appreciable displacement of atoms from their unperturbed positions in the perfect virtual crystal. Such displacements dramatically affect intensity of diffracted electron beams when performing DF imaging.<sup>4</sup> We will compare the composition derived for Ga(NAs)/GaAs quantum wells in the concentration range of 0 to 10% N by 002 DF TEM to the composition obtained from other methods; for example, high-resolution x-ray dif-

fraction (HRXRD) of the (004) reflection and dynamical simulations to those diffraction patterns. Regarding XRD, the tetragonal distortion of the Ga(NAs) with respect to the GaAs substrate is used to extract the chemical composition from the (004) reflection assuming Vegard's law and the evaluation is negligibly influenced by static displacements of atoms, as the macroscopic, tetragonally distorted lattice constant is extracted directly from the XRD measurement and no fitting of reflection intensity to some theoretical value takes place. It will be shown that disregarding the influence of static displacements on the structure factor results in a strong underestimate of the N content in the quantum wells, if the intensity of chemically sensitive reflections is used to gain this information. These findings have an important impact on the quantification of nanoanalytical TEM, influencing the 002 dark-field imaging as well as high-resolution imaging of this class of materials as the 002 beam also contributes to most HR images.

Ga(NAs)/GaAs multi-quantum-well structures have been grown by metalorganic vapor phase epitaxy (MOVPE) in a commercial reactor system (AIX200-GFR) under  $\text{H}_2$  carrier gas at a reduced pressure of 50 hPa. As one deals with a metastable material system nonequilibrium growth conditions, low substrate temperatures have to be employed, and hence the more efficiently decomposing group V precursors (tertiary butyl arsine and 1,1-dimethylhydrazine) have been used. The TEM structures were multi-quantum-well structures, having GaAs barriers 100 nm wide in order to ensure that any strain contrast caused by the deformation of the thin TEM sample and even visible in 002 dark-field images does not influence the subsequent quantum well intensity. Different N contents were achieved by changing the ratio of the partial pressures of the group V sources. To be able to independently calibrate the N content of the samples HRXRD (004) rocking curves have been measured and simulated using dynamical diffraction theory. The elastic constants used to calculate the N content from the strained layer XRD signal

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assuming Vegard's law, have been taken from Ref. 5 and were as follows. GaAs:  $c_{11}=121.1$  GPa;  $c_{12}=56.6$  GPa; GaN:  $c_{11}=293$  GPa;  $c_{12}=159$  GPa. For the elastic constants of the ternary alloy, a linear interpolation between the GaAs and GaN values has again been assumed, neglecting any bowing of the elastic constants as recently suggested by Ref. 6. The validity of Vegard's law for the samples investigated in this study as well as the justification for neglecting the bowing of the elastic constants for the MOVPE grown samples under investigation here, have been confirmed by performing calibrated secondary ion mass spectrometric investigations on selected Ga(NAs) samples, using a N ion implanted GaAs wafer as a calibration reference. [010] TEM cross sections were prepared by mechanical polishing followed by 3 kV and 1 kV Ar ion milling as well as by cleavage techniques. The  $g=(002)$  dark-field images were obtained in a Jeol JEM3010 at an acceleration voltage of 300 kV, tilting the samples around the growth direction away from the [010] pole so that only the transmitted beam and the 002 beam were excited strongly. In the geometry used, the center of Laue circle corresponded to (20,0,1.5) for the (002) reflection, resulting in low influence of small thickness fluctuations of the samples on the observed image intensity.

For the theoretical calculation of the scattering intensities the method suggested recently by Glas<sup>4</sup> has been used. We also took into account macroscopic strain caused by the lattice mismatch between the Ga(NAs) quantum well and the GaAs barriers leading to a tetragonal distortion of the unit cell. The kinematical scattering intensity of the incident electron beam is proportional to the squared absolute value of a structure factor:  $I(\mathbf{g}) \propto |F(\mathbf{g})|^2$ . Taking into account the static atomic displacements, the average value of the structure factor for the particular reflection  $\mathbf{g}=(hkl)$  can be expressed in the form

$$F(\mathbf{g}) = N^{-1} \left\{ \sum_j f_j(\mathbf{g}) \exp[2\pi i \mathbf{g} \cdot (\mathbf{r}_j + \mathbf{u}_j)] \right\}, \quad (1)$$

where  $N$  is the number of unit cells over which we average the structure factor,  $f_j(\mathbf{g})$  is the kinematic electron scattering factors,  $\mathbf{u}_j$  is the vector of static displacements of atoms from the average crystal sites  $\mathbf{r}_j$ . The form of Eq. (1) implies that group V atoms occupy sites with coordinates  $\mathbf{r}^{(V)}=(0,0,0)$ , whereas group III atoms are located at  $\mathbf{r}^{(III)}=(0.25,0.25,0.25)$ . The kinematic electron scattering factors for individual atoms calculated by Doyle and Turner<sup>7</sup> have been used. In order to compute the atomic displacements ( $\mathbf{u}_j$ ) we employ the valence force field (VFF) supercell method used previously by Glas.<sup>4</sup> We used a supercell of the size  $20 \times 20 \times 20$  unit cells, showing adequate convergence for the structure factor. We first placed the atomic species at their "ideal" positions ( $\mathbf{r}_j$ ), in the virtual crystal taking into account the tetragonal distortion. We then relaxed the atomic coordinates with respect to the total strain energy in accordance with Keating's valence force field model.<sup>8</sup> Interaction parameters for GaAs and GaN used in the strain energy functional are listed in Ref. 9. During the relaxation procedure we applied additional constraints in order to keep the macroscopic strain of the supercell constant. The relaxed atomic positions, ( $\mathbf{r}'_j$ ), are used to evaluate the components of displacement vector in the form  $\mathbf{u}_j=(\mathbf{r}_j-\mathbf{r}'_j)$ . The displacement vectors, ( $\mathbf{u}_j$ ) of each atomic species are used in order to

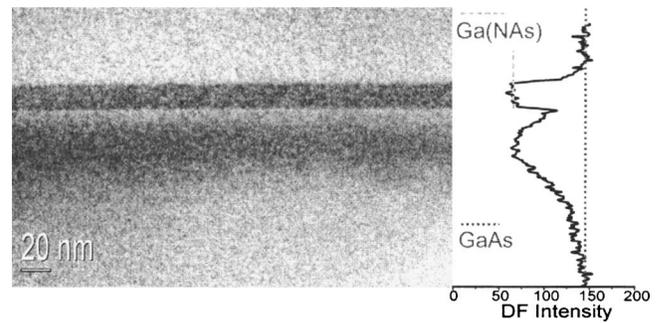


FIG. 1. Dark-field TEM image [ $g=(200)$ ] from a Ga(NAs)/GaAs quantum well. The N content from XRD was 9.6%. A line scan across the image is shown on the right-hand side with the intensity levels of the Ga(NAs) and GaAs indicated.

compute the average structure factor from Eq. (1). The structure factor has been calculated for tetragonally strained material for the (002) as well as for the (200) reflection. In order to be able to use the values calculated also for other microscopes, for example, ones operating at a different acceleration voltage, the intensities to be expected for the respective reflections have been normed to the GaAs values and can hence be used independently of the setup.

The 002 DF images of the Ga(NAs) show a specific contrast structure in the growth direction and if quantitative results are to be extracted, extreme care should be taken to use appropriate imaging conditions as well as optimum prepared TEM samples, which have large electron transparent regions with equal thickness. For N concentrations in the range investigated here, the Ga(NAs) QWs have a darker contrast in 002 DF images compared to the GaAs matrix, as is, for instance, shown in Fig. 1 for a structure having a N content of 9.6% (from XRD). From the homogeneous contrast in the growth plane, parallel to the interfaces of the QW, we conclude that there are no chemical inhomogeneities present in plane. Adjacent to the QW in the GaAs substrate we always find—despite imaging with a so-called chemical sensitive reflection—a darker contrast, which is caused by the strain field of the QW. Similar signals have been observed before for (GaIn)As/GaAs QWs.<sup>10</sup> One can clearly recognize the described contrast structure in the line scan across the image, which is also shown in Fig. 1. The N content has been determined by normalizing the Ga(NAs) intensity to the GaAs intensity. Those two intensities are indicated in the line scan as dashed and dotted lines, respectively. Extreme care has to be taken to use the correct GaAs intensity due to the large influence of the strain. Differently thick sample regions as well as also cleaved samples have been examined to ensure that one yields identical intensity ratios for structures of the same composition. This confirms that strain and chemical contrast are indeed not superimposing each other. The intensity ratios have been compared to the ratios of the squares of the absolute values of the structure factors of GaAs and Ga(NAs) with different N contents. At the beginning a perfect average crystal has been assumed. Structure factors have been calculated using Eq. (1) and setting  $\mathbf{u}_j$  equal zero. This yields the open symbols in Fig. 2. As we calculated assuming a tetragonally distorted Ga(NAs) cell on GaAs, the (002) and (200) planes become nonequivalent. The squared and round symbols represent the data for those two directions. For the perfect average—virtual—crystal (open symbols) the difference between the signals is cer-

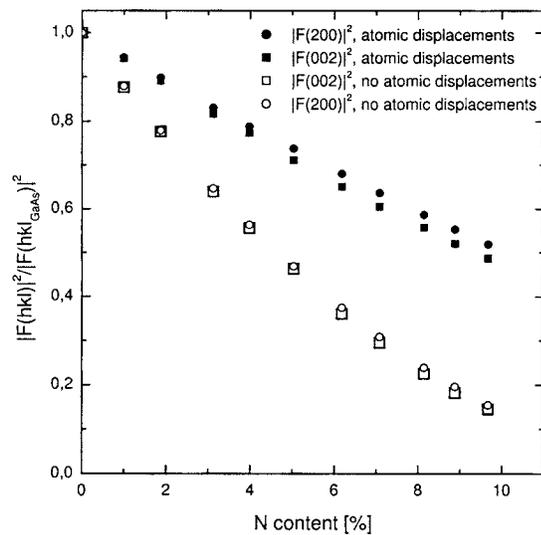


FIG. 2. Compositional dependence of the structure factor for {002} reflections in tetragonally distorted Ga(NAs). The values have been normalized to the respective GaAs values. The filled and open symbols correspond to the results including static atomic displacements and without them, respectively. The growth direction is [001].

tainly within the error bar. Drastically different intensities are observed when the atomic displacements caused by the N are taken into account when calculating the structure factor (full symbols).

The N compositions calculated assuming the virtual average unit cell are compared to that ones from HRXRD analysis of the (004) reflection in Fig. 3 (open symbols). The TEM dark-field evaluation in comparison to the one from XRD clearly underestimates the N content in the samples. The error bars of the TEM evaluation include all the contrast values that have been derived from differently thick sample regions as well as differently prepared samples. The error bar which has to be attributed to the XRD measurement is rather small and amounts—for ternary material—to  $\pm 0.2\%$  N absolutely. This error is caused mainly by the possible error in determining the position of the envelope of the Ga(NAs)

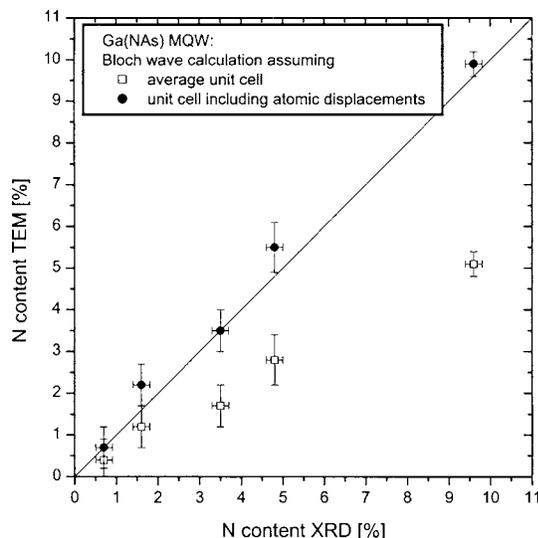


FIG. 3. Comparison of the N content in Ga(NAs)/GaAs quantum wells derived from TEM and XRD analysis, respectively. The filled and open symbols correspond to structure factors calculated taking static atomic displacements into account and disregarding them, respectively.

signal in the XRD measurements. As the values for the N content of the samples between XRD and TEM disagree beyond the error bars, we recalculated the structure factors of Ga(NAs) assuming the static displacements the N causes according to Eq. (1), now using the  $u_j$  values from our VFF calculation. The result for this structure factor calculation is shown as the filled symbols in Fig. 2. The square of the absolute value of the structure factor including displacements is significantly higher than the one without displacements also implying a lower contrast ratio of the Ga(NAs) normalized to the GaAs value in the 002 DFs. One also recognizes that the contrast ratio using the reflection corresponding to the growth planes is slightly higher than the one of the perpendicular (200) planes. Using the structure factors, which take the locally relaxed unit cell into account, to calculate the N content one ends up with the filled symbols in Fig. 3, now having an almost perfect agreement between the N contents from XRD and TEM analysis. The results could be further refined if electron scattering factors were not taken in single atom approximation but be possibly calculated by using density functional theory as has been shown to improve the accuracy for (GaIn)As before.<sup>11</sup>

In summary, we have grown specific Ga(NAs)/GaAs multi-quantum-well structures having different N contents. These samples were analyzed by 002 dark-field transmission electron microscopy as well a high-resolution x-ray diffraction, including dynamical simulation of the XRD patterns. We find that assuming an average crystal for structure factor calculations of the Ga(NAs) in the range of N contents up to 10% strongly underestimates the N concentration derived from DF TEM analysis as compared to the one obtained from XRD. Taking static atomic displacements into account by relaxing the crystals using valence force field methods, we find that the results from TEM analysis are in quantitative agreement with the ones from XRD. It is of key importance, if quantitative information is to be extracted from TEM images using so called chemically sensitive reflections, to take relaxation of the unit cell on an atomic level into account, especially if elements with strongly different covalent radii are mixed. This study establishes a basis for quantitative nanostructural analysis of dilute N containing materials using either 002 dark-field imaging or high-resolution imaging, where these reflections are included to form the image.

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