Simultaneous determination of local thickness and composition for ternary III-V semiconductors by aberration-corrected STEM

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Abstract

Scanning transmission electron microscopy (STEM) is a suitable method for the quantitative characterization of nanomaterials. For an absolute composition determination on an atomic scale, the thickness of the specimen has to be known locally with high accuracy. Here, we propose a method to determine both thickness and composition of ternary III-V semiconductors locally from one STEM image as shown for the example material systems *Ga(AsBi)* and *(GaIn)As*. In a simulation study, the feasibility of the method is proven and the influence of specimen thickness and detector angles used is investigated. An application to an experimental STEM image of a *Ga(AsBi)* quantum well grown by metal organic vapour phase epitaxy yields an excellent agreement with composition results from high resolution x-ray diffraction.

1. Introduction

Scanning transmission electron microscopy (STEM) became a widely used technique for the atomic-scale analysis of nanomaterials, especially technologically relevant ones. For the optimization of these nanomaterials, the atomic-scale characterization by STEM plays an important role in the interplay of theoretical predictions, growth and material characterization with the aim of improving the performance of the final device.

In particular, annular dark field (ADF) STEM proved to be suited for a quantitative analysis of material properties that includes locating, counting and distinguishing atoms in a material matrix. To achieve these goals, two main ideas were established. One is based on imaging models with statistical parameter estimation theory and the other one relies on the comparison of experimental and simulated images.

With the former one, relative composition determination [1] and atom counting with single atom sensitivity [2] were accomplished. By combining the statistical framework with image simulations, atom counting could be further improved [3] and atomic-scale composition determination was brought to an absolute scale [4]. Additionally, for composition determination on an atomic scale, an atomic lensing model was developed [5,6].

The direct comparison of experimental and simulated image intensities will be discussed in more detail since this is the ansatz followed in this work.

For this direct comparison of experimental and simulated image intensities, a normalisation of the intensities to the impinging electron beam is crucial [7]. To be able to analyse each atomic column separately, pixel intensities are assigned to the atomic columns which could either be done by circular integration [8], Voronoi intensities [9] or pixel integrated cross sections [10].

For highest accuracy in the comparison of experimental and simulated intensities, electron probe, specimen, probe-specimen interaction and detector have to be known and modelled precisely. In case of the electron probe, this especially includes the effect of chromatic aberration [11] and of a finite source size [12–14] and coherent lens aberrations [15]. Static atomic displacements [16], strain [17], tilt [18], surface relaxation [19,20] and amorphous layers [21–23] are characteristics of the specimen that influence ADF-STEM image intensities. Alongside a general knowledge of the probe-specimen interaction [24,25], especially the influence of thermal diffuse scattering [26,27] is of importance.

For the electron detector, next to the general geometry [28], the detector angles [7] and the non-uniform detector sensitivity [7,29,30] influence experimental results.

Taking into account all these parameters, atom counting [31] and composition determination can be conducted. Composition determination was performed on non-atomic [30] and atomic scale [9,32,33] for III-V semiconductors.

To be able to determine absolute atomic scale composition, the specimen thickness has to be known locally. Already small thickness deviations can make accurate, i.e. single-atom accuracy, composition determination impossible depending on the material system [33]. Determination of local thickness is normally achieved by an inter- or extrapolation of thickness in regions with known composition [9,30] but this will obviously lead to local thickness deviations. Another possibility is the usage of atomic columns with known composition being justified by a small influence of cross-

scattering due to small specimen thicknesses but failing for thicker specimens [4,33]. Furthermore, a method was developed where the composition and thickness characteristic electron scattering was detected in two ADF-STEM images taken at different angular ranges [32]. Complementary methods for thickness determination like electron energy loss spectroscopy [34] or convergent beam electron diffraction [35] do not offer the necessary accuracy or have other limitations.

In this work, we propose a method to simultaneously determine the local thickness and composition for ternary III-V semiconductors from a single ADF-STEM image using complementary image simulations. For the composition determination, the sub lattice where the matrix atom is replaced by the substitute atom is utilized while for thickness determination the other sub lattice with known composition is employed. The latter is prevented by the influence of cross-scattering at a certain thickness. However, this influence and the knowledge about it drawn from simulation is used to determine thickness and composition locally on an atomic scale. This process is performed iteratively analysing both sub lattices separately.

For this, the outline is as follows: After general information about STEM image simulations and experimental setups, the method itself is explained in detail. Then, a proof of principle is given by applying the method to a simulated STEM image of *Ga(AsBi)* which is a promising material for optoelectronic applications and for which the composition is fully known. Additionally, it is also applied to a simulated STEM image of *(GaIn)As*. In a simulation study, the influence of detector angles and specimen thickness are investigated leading to preferred conditions that are considered for applying the method to experimental STEM images of a *Ga(AsBi)*-QW grown by metal organic vapour phase epitaxy (MOVPE). Finally, the obtained results are discussed.

2. STEM image simulations

STEM image simulations are performed for quantitative evaluation of STEM image intensities. For this, the software package STEMsalabim [36] is employed.

STEMsalabim is based on the multi slice algorithm [37] and optimized to run on parallelized computing clusters. Thermal diffuse scattering is included by the frozen phonon approximation [27] and a defocus series [11] of seven different defoci centred around $\Delta f = 0$ nm with a full width half maximum of 7.5 nm considers the effect of chromatic aberration. A detector scan allows to consider the non-uniform

detector sensitivity [7,9,29,30]. The finite source size is built in by a Lorentzian convolution [14] for which the width is carefully adjusted. All parameters for image simulations are chosen in accordance with the microscope at hand and are summarized in Table I.

Super cells are generated for $Ga(AsBi)$ with a varying average Bi concentration of $x = 0, 0.02, 0.04, \dots, 0.14$ and a size of $5 \times 5 \times 80$ unit cells ($x \times y \times z$). Thereby, Bi atoms are statistically distributed inside the super cell. Slicing of the super cell was done in a way that one slice contains one atom per atomic column. A valence force field relaxation of Keating's potential [38] takes into account the effect of static atomic displacements. For $Ga(AsBi)$, 700 group V and 567 group III atomic columns are evaluated. Equivalent image simulations are also performed for $(GaIn)As$ with an average In composition varying from $x = 0, 0.05, 0.10, \dots, 0.50$. Here, 539 group III and 704 group V atomic columns are evaluated.

Electron energy	200 kV
Aperture angle	21.3 mrad
Astigmatism	0 nm
C_s	2 μm
C_5	5 mm
C_c	1.5 mm

Table 1: Parameters for STEM image simulations as determined for the microscope at hand

3. Experimental

The $Ga(AsBi)/GaAs$ multi quantum well (MQW) structure was grown in an Aixtron AIX 200 reactor with gas foil rotation. The reactor pressure was kept constant at 50 mbar and H_2 was used as carrier gas. For growth at low temperatures Triethylgallium ($Ga(C_2H_5)_3$), Tertiarybutylarsine ($As(C_4H_9)H_2$) and Trimethylbismuth ($Bi(CH_3)_3$) were chosen as *Gallium*, *Arsenic* and *Bismuth* source, respectively. First, a $GaAs$ buffer layer was deposited at 625 °C on top of the exact n^+ - $GaAs$ substrate to ensure a smooth growth surface. The $Ga(AsBi)$ quantum well (QW) was grown at a reduced growth temperature of 400 °C whilst the barrier was grown at 550 °C to prevent segregation of Bi into the $GaAs$ barrier [39]. Growth interruptions between the layers were established to change the growth temperature of the layer, respectively. Multi QW thickness and strain were determined by simulation of a high-resolution X-Ray (HR-XRD) diffractogram around the (004)-reflection. Using a $GaBi$ lattice constant of 6.33 Å [40], the Bi fraction was calculated to 5.8% from the strain. The

QW thicknesses were determined to 7.2 nm separated by 34.9 nm thick GaAs barriers.

For TEM investigations, a cross-sectional lamella was prepared of this sample using a dual beam scanning electron microscope focused ion beam (FIB) machine (JEOL JIB-4601F, JEOL Ltd., Tokyo, Japan). Applied milling voltages for the *Ga* ions were progressively reduced from 30 kV to 10 kV. The specimen thickness after this initial FIB preparation was roughly 140 nm.

Further sample thinning was performed using a NanoMill® TEM specimen preparation system (model 1040, E. A. Fischione Instruments, Inc., Export, PA, United States) [41] using a milling voltage of 900 eV for the *Ar* ions utilized. Milling was continued with an inclination angle of $\pm 10^\circ$ until the final specimen thicknesses were reached.

STEM measurements were realized with an aberration-corrected JEOL JEM 2200FS (JEOL Ltd., Tokyo, Japan) operating at 200 kV acceleration voltage. Electrons scattered into an angular range of 67-268 mrad were detected by the annular dark-field detector (JEOL EM-24590YPDFI). The inner detector angle was determined according to [7] while the outer detector angle is determined by the geometry of the detector. A convergence angle of 21 mrad was used resulting from a condenser aperture with a diameter of 40 μm . The hexapole lenses of the imaging corrector were turned off to avoid a cut-off in the diffraction plane [42]. Images were recorded as a stack of 10 images with a dwell time of 3 μs and aligned afterwards using the SmartAlign software [43] to reduce the influence of sample drift and scan distortions. For comparison with simulated STEM images, image intensities were normalized to the impinging electron beam [44]. Peak position finding in the STEM images was achieved by applying the peak finding software PeakPairs [45].

4. Method

In the following, we describe the method developed to determine thickness and composition simultaneously for ternary III-V semiconductors using an STEM image.

The first crucial step is to fix the width of the Lorentzian convolution needed to take into account the finite source size for all following simulations. For a given experimental image, this is achieved by a pixel wise comparison of a simulated and

an experimental average unit cell at the same thickness. In detail, this procedure can be found in [33].

Voronoi intensities [9] are assigned to every atomic column of the experimental image and will also be used for simulations. They are chosen as they are robust against surface relaxation that can strongly influence STEM intensities in semiconductor heterostructures [19,20].

Then, the thickness of every atomic column is determined initially. This is achieved by the comparison of the Voronoi intensities of every atomic column of the sub lattice with known composition with simulated Voronoi intensities of the same sub lattice in the matrix material. Hence, in the case of *Ga(AsBi)* group III atomic columns containing only *Ga* atoms are compared to simulated group III atomic columns in a *GaAs* super cell. By this comparison, the thickness of every atomic column can be fixed given in number of atoms in this column. The thickness of group V atomic columns with unknown composition is found by averaging the thickness of the 4 next neighbour (NN) group III atomic columns that are present in [010]-direction that is used.

After this initial thickness determination, a first initial composition determination can be performed. The obtained intensity composition relationship is shown in Fig. 1(a). For this, for all thicknesses present in the experimental image the simulated super cells with varying *Bi* concentration have to be evaluated. For every group V atomic column, the number of *Bi* atoms contained in this column and the Voronoi intensity is read. Because of different z-heights of *Bi* atoms within each atomic column, this leads to an intensity distribution for every *Bi* composition. However, a mean Voronoi intensity can be determined for every *Bi* composition that will be used to determine the *Bi* composition of every experimental atomic column by comparison of Voronoi intensities. This is also described in more detail in [33].

With this initially determined composition, the thickness can be determined again. For this, the simulated super cells with varying *Bi* concentration are evaluated in a different way. Using a range of thicknesses, for every group III atomic column the Voronoi intensity together with the columns thickness and the average NN *Bi* composition is read. Again this gives a distribution of Voronoi intensities for every NN composition for which a mean value is found. This dependency between intensity and average NN *Bi* composition for group III atomic columns is shown in Fig. 1(b).

The thickness of every group III column in the experimental image can then be determined by comparison to simulated Voronoi intensities considering the average NN Bi composition that was determined in the step before. Then, the thickness of group V atomic columns is again determined by averaging the thickness of NN group III atomic columns.

Fig. 1: Relationship between group V Voronoi intensity and Bi composition (a) and group III Voronoi intensity and average NN Bi composition (b) for $GaAsBi$ at a total thickness of 30 atoms per atomic column. For both cases, all events within the simulated super cell (blue) are shown together with the mean intensity (red).

With these adapted thicknesses, the Bi composition of group V atomic column is again determined by comparison to simulation as described before.

These last two steps are performed iteratively until a stable thickness composition configuration is found. For the simulated cases investigated, this was always the case after five iterations.

5. Proof of principle using simulated STEM image

To prove the feasibility of the method described above, it will first be applied to a simulated STEM image for which the super cell and its composition generating this image are fully known. Hence, one can compare thickness and composition obtained to the real values for every atomic column.

For this, a super cell with a composition of $GaAs_{0.94}Bi_{0.06}$ is chosen with a thickness of 30 atoms in every atomic column. To generate the STEM image, a virtual detector range of 70 to 280 mrad is chosen and the experimentally obtained non-uniform detector sensitivity is applied to closely resemble the experiment. A Lorentzian

convolution with a width of $\sigma = 0.05$ nm is applied in accordance with experimental conditions. The resulting STEM image is shown in Fig. 2(a). First, the initial thickness determination is performed as described above and the resulting thickness map is shown in Fig. 2(b) for the group V columns only. Note, that atomic columns at the edges are removed due to incomplete, open Voronoi cells and unfulfilled NN relationships. As can be seen, the thickness is generally overestimated by 1 to 2 atoms since the intensity of group III atomic columns is increased compared to GaAs due to the influence of cross scattering from group V atomic columns. The thickness is determined correctly only for 40% of the 81 group V atomic columns highlighting the necessity of taking cross scattering into account at this thickness.

The initial composition map resulting from this initial thickness determination is shown in Fig. 2(c). Due to the generally overestimated thickness of atomic columns, the *Bi* composition is generally underestimated. Though, the *Bi* composition is still determined correctly for 56% of the group V atomic columns. This leads to a total deviation of -35 *Bi* atoms compared to the real composition in the simulated super cell that contains 140 *Bi* atoms. The column wise deviation to the real composition is shown in Fig. 2(d).

Fig. 2: (a) Simulated STEM image of GaAsBi containing 6 % Bi at a thickness of 30 atoms per atomic column. (b) Thickness of group V atomic column determined initially via the group III sub lattice and comparison of Voronoi intensities to simulations. (c) Bi composition determined at the thicknesses shown in (b) by comparing to intensity composition relationships. (d) Deviation of determined composition shown in (c) to the real composition of the super cell. When comparing

STEM image in (a) and column representations in (b)-(d) note that only group V atomic columns are shown and edge regions of the image are excluded.

After three cycles of iteratively determining the thickness of every atomic column considering the Bi composition derived before and the composition of every atomic column considering the current thickness, the configuration of thickness and *Bi* composition is stable. The resulting thickness, composition and composition deviation maps are shown in Fig. 3(a), (b) and (c), respectively. The thickness is determined correctly for all but one column (99%) while the *Bi* composition is correct for 78 % of the columns. The summed total deviation of *Bi* atoms is +2 for the 140 *Bi* atoms contained in the super cell so the total composition is well reflected.

Fig. 3: Thickness (a), Bi composition (b) and deviation to the real composition (c) for the same simulated STEM image shown in 2(a) after applying the proposed method for thickness and composition determination with 5 cycles.

As a comparison, the composition is also determined for that case if the thickness of all atomic columns is known correctly. In this case, the composition is determined for 79% of the group V atomic columns and the total deviation is -1 *Bi* atom. Hence, the method introduced above essentially reaches the inherently present limitations of this composition determination via comparison to mean Voronoi intensities of atomic columns. These limitations exist due to different z-height distributions of the substitute (*Bi*) atoms inside the atomic columns and following different intensities. However, these limitations are of statistical nature and are discussed in detail later on.

To show that the proposed method is not only working in the special case of *Ga(AsBi)*, it is also applied to a simulated STEM image of $(Ga_{0.7}In_{0.3})As$ at a thickness of 35 atoms per atomic column and detector angles of 70 to 280 mrad (Fig.

4). With the proposed method, the thickness is determined correctly for 92% of 49 group III atomic columns which leads to a composition determination that is correct in 33% of the group III atomic columns. The overall deviation of the composition is 4 *In* atoms for 495 *In* atoms contained in the super cell. If the thickness is known correctly for every atomic column the composition is determined correctly for 33% of the group III atomic columns and a deviation of 4 *In* atoms which is dictated by the statistical nature of composition determination. Hence, the same accuracy is reached with the method proposed.

For now, it is concluded that the method introduced allows us to determine thickness and composition of the atomic columns shown in the simulated STEM images with good accuracy.

Fig. 4: STEM image of $(Ga_{0.7}In_{0.3})As$ for a thickness of 35 atoms per atomic column (a), together with the thickness (b), the composition (c) and the deviation to the real composition (d) determined by applying the proposed method. When comparing STEM image in (a) and column representations in (b)-(d) note that only group III atomic columns are shown and edge regions of the image are excluded.

6. Influence of detector range and specimen thickness

To get a more comprehensive understanding of the method described, the influence of the detector range employed and of specimen thickness are investigated in a simulation study. For this purpose, the proof of principle described for the simulated STEM image above in detail is performed for the $\text{GaAs}_{0.94}\text{Bi}_{0.06}$ super cell but with varying thickness and images recorded with different virtual detector ranges.

Specimen thicknesses range from 10 to 60 atoms per atomic column in steps of 5 atoms per atomic column while for every thickness inner detector angles from 30 mrad to 100 mrad in steps of 10 mrad were evaluated. The outer detector angle was chosen as four times the inner detector angle which corresponds to the geometry of the detector used in this work. A maximum simulation angle of 300 mrad was chosen since intensity scattered to higher angles hardly effects the intensity finally collected by the detector because of the θ^{-4} dependency of the scattered intensity.

For each thickness-detector configuration, we evaluated the total deviation of *Bi* atoms between determined and real composition and the percentage of correctly determined columns for both composition and thickness.

In a first step, for a given thickness of 30 atoms per atomic column the influence of the detector range is evaluated. The results are shown in Fig. 4(a) for the total deviation of *Bi* atoms and the percentages of correctly determined atomic columns. With increasing inner detector angle from 30 mrad to 70 mrad, the total deviation to the real composition tends to zero while the number of correctly determined columns increases for both thickness and composition. For inner detector angles of 70 mrad and 80 mrad, thicknesses are determined correctly for almost every atomic column while this leads to the composition being determined correctly in almost 80% of the cases. The total deviation of the composition is 2 *Bi* atoms for both detector ranges. Increasing the inner detector angle leads to a decline in correctly determined atomic columns and an increase in the deviation. Hence, experimentally one should aim to work with an inner detector angle of 70 to 80 mrad for the given thickness of 30 atoms per atomic column.

Secondly, it is investigated whether the proposed method is working for every thickness range. Thicknesses are investigated up to 35 atoms per atomic column. Up to this thickness, for the given super cell size edge effects can be excluded. In Fig.

4(b), the absolute total deviation between the real and the determined *Bi* composition together with the percentage of correctly determined atomic columns for both thickness and composition is shown. For very thin samples up to 20 atoms per atomic column composition and thickness can be determined correctly for (almost)

Fig. 5: Detector angle dependency of the proposed method for a super cell of *Ga(AsBi)* with 6% *Bi* and a thickness of 30 atoms (a). Thickness dependency of the proposed method for the same super cell (b). In a simulation study, the deviation of the total *Bi* composition determined to the real composition of the super cell (black) and the fraction of group V atomic columns for which the composition (red) and the thickness (blue) were determined correctly were analysed.

every atomic column, whereas this percentage decreases with increasing thickness afterwards. However, up to a thickness of 30 atoms per atomic column the total composition can be deduced accurately with a deviation of only 2 *Bi* atoms, at most. For a thickness of 35 atoms per atomic column, the deviation to the real composition increases to 7 *Bi* atoms and the percentage of correctly determined columns drops to 73% while the thickness is determined for 94% of the atomic columns. However, with 2835 group V atoms and 163 *Bi* atoms in the super cell the absolute concentration deviation is only 0.2%.

Hence, for all investigated thicknesses the proposed method works accurately for the total composition but the local accuracy decreases. The thickness of every atomic column can be determined with 99% accuracy up to a thickness of 30 atoms per atomic column. For taking experimental STEM images, working in specimen regions with a thickness of 35 atoms per atomic column (~20 nm) is possible depending on the goal of the investigation. If one is interested in high local accuracy for the composition determination in contrast to a more global information, thinner

specimens have to be investigated. This has to be considered for sample preparation but is definitely achievable experimentally.

7. Application to experimental STEM image

The proposed method was also applied to an experimental STEM image of a *Ga(AsBi)*-QW with *GaAs* barriers grown on a *GaAs* substrate for which the composition is known from HR-XRD measurements. For acquiring the STEM image, the detector range was chosen as 67-268 mrad which is in agreement with the optimal detector range determined by the simulation study above. Additionally, we aimed for a specimen thickness below the upper limit of 20 nm which was also ascertained above.

The STEM image of the *Ga(AsBi)*-QW is shown in Fig. 5(a) already being normalized to the impinging electron beam. Here, the *Ga(AsBi)*-QW is on the left side of the image while on the right side *GaAs* is present. The small field of view due to high magnification is sufficient since no binary reference material is needed on both sides of the QW. The method proposed was applied with 15 thickness-composition refinement steps to this image. The resulting thickness map is shown in Fig. 5(b). As can be seen, the thickness of the atomic columns ranges from 26 to 31 atoms per column and therefore is below the thickness limit of 35 atoms per atomic column discussed before. Using this thickness map for composition determination, the composition map presented in Fig 5(c) was retrieved. For the composition determination, the intensity composition relationships were extrapolated to negative compositions of *Bi* both for on- and off-column relationships to take into account the possibility of experimental noise. Resulting compositions range from -1 to 6 *Bi* atoms per atomic column clearly showing that the QW just begins on the left side of the image and that there is *GaAs* on the right side of the image. Within the QW, also clustering of *Bi* atoms is apparent which was reported for this material system before [8].

By averaging over the lattice planes in the vertical direction, i.e. parallel to the interface, a composition profile of the *Ga(AsBi)*-QW is generated. To take into account the differing thickness of atomic columns and enable a comparison, *Bi*

composition is given as concentration. The resulting concentration profile is shown in Fig. 5(d) (red profile). Here, it has to be noted that the shaded region does not show the error of the composition determination but rather the standard deviation of the concentration along one lattice plane that contains 34 atomic columns in the present case. Additionally, the concentration profile that would result from an initial thickness

Fig. 6: Application of the proposed method to an STEM image of a GaAsBi-QW grown by MOVPE. The STEM image (a) shows the GaAsBi-QW on the left and GaAs barrier on the right. Thickness map (b) after 15 iterative cycles. Composition map (c) for thicknesses shown in (b). The QW is clearly distinguishable. Concentration profile (d) of the initial (blue) and final (red) composition determination together with its standard deviation within one lattice plane (shaded red). For comparison reasons, also the concentration profile as determined by HR-XRD (black) is shown.

and composition determination without applying the refinement steps is given (blue profile). For comparison purposes, the initial thickness and composition maps are added as supporting information. Finally, also the concentration profile obtained by HR-XRD is shown in Fig. 5(d) (black profile). A comparison between the final concentration profile obtained and the box-like concentration profile obtained by HR-XRD with a QW width of 7.2 nm and a *Bi* concentration of 5.8 % yields a very good agreement and therefore confirms the validity of the method also experimentally. In

contrast, the concentration profile resulting from the initial composition determination distinctly differs from the HR-XRD profile and the final concentration profile and underestimates the *Bi* concentration due to overestimating the thickness of the atomic columns.

8. Discussion

In the following, the proposed method and its application is discussed regarding several aspects. This starts with the method in general and its statistical character as well as its accuracy. Then the best imaging conditions for a successful composition determination and the experimental results are explained.

The proposed method was developed out of the need for an accurate knowledge of the thickness of every atomic column in order to determine its thickness. As was shown in [33], already a difference between the assumed thickness and the real thickness of one atom per atomic column leads to an incorrect composition determination in most cases. Hence, a correct knowledge about the thickness is crucial to determine the composition with atomic accuracy and avoid to make assumptions of the thickness in the region with unknown composition [9,30,33]. Furthermore, the method proposed works with only one STEM image detected for one detector range in comparison to the angular resolved STEM ansatz [32] that detects composition and thickness characteristic scattering at different angular ranges.

Cross-scattering limits the use of the sub lattice with constant composition in ternary III-V semiconductors for thickness determination to very small thicknesses (10-15 atoms per atomic column in the case of *Ga(AsBi)*) as for these the influence of cross scattering is marginal. For the proposed method, it is this existence of cross-scattering that is exploited by reading this information from image simulations. These image simulations are at the heart of simulation-based quantitative STEM analysis and therefore an exact modelling of probe, specimen and detector is necessary. By using the iterative composition and thickness determination described above, an ensemble of a cohesive thickness and composition configurations can be found.

Thereby, the composition determination has a strong statistical character as discussed in detail in [33]. For a given thickness, for every quantity of substitute

atoms in an atomic column an intensity distribution arises due to different possible z-configurations of these substitute atoms, i.e. z-heights with respect to the impinging beam. These intensity distributions have a certain overlap depending on material system, specimen thickness and number of substitute atoms. However, for the evaluation these intensity distributions are only represented by mean values that inherently lead to errors in composition determination for extremal z distributions. For example, atoms placed on top of the column will have a higher intensity than the mean intensity for this composition and vice versa. Nonetheless, on average this composition determination still yields the correct value given a large enough value of atomic columns to evaluate. For the simulation study presented above, only 81 atomic columns out of one super cell were evaluated but for experimental images there are typically several thousand atomic columns within one image (1098 group V atomic columns in the experimental STEM image used). Hence, the statistically determined mean value for the composition is still correct.

The percentage of atomic columns for which the composition is determined correctly, i.e. the exact number of substitute atoms in that column, decreases with increasing thickness since with increasing thickness there are more possibilities to arrange a given number of substitute atoms within one column and overlap between the resulting intensity distributions increases. This decreasing percentage of atomic columns for which the composition can be determined correctly also leads to a decreasing percentage of atomic columns for which the thickness can be determined correctly. The thickness determination depends on the average NN composition that is not correct anymore. Hence, the thickness is not correct anymore which then leads to a wrong composition of that atomic column as the thickness is crucial. This explains why the performance of the method proposed decreases with increasing thickness as found in the simulation study.

Therefore, the statistical character of the experimental method prevents a correct composition determination of every single atomic column whereas the overall composition is determined correctly given a large enough number of atomic columns. These effects are then exaggerated for the simultaneous thickness and composition determination as these two characteristics are strongly mutually dependent.

The fact that the composition of an atomic column is not determined correctly for 100% of the atomic columns also leads to the necessity to assess the accuracy of the

present method. As previously explained, this accuracy depends on the overlap of the intensity distributions that for a given material system increases both with increasing thickness and composition. Hence, these three factors have to be considered when determining the accuracy of the proposed method. One way to assess this accuracy is an evaluation of the results of the simulation study. For the super cell with a *Bi* concentration of 6% (140 *Bi* atoms of 2430 total group V atoms) and a thickness of 30 atoms per atomic column that closely resembles the experimentally investigated QW, the detailed evaluation performed above yielded deviations of ± 1 *Bi* atom for 22% of the atomic columns while for 78% of the atomic columns the composition was determined correctly. Since the *Bi* atoms were statistically distributed within the super cell, this value of 78% correctly determined atomic columns and an error ± 1 *Bi* atom for the remaining atomic columns can be assumed to reflect the accuracy of the given combination of material system, thickness, and composition.

The influence of the material system on the accuracy of composition determination manifests itself through the difference in atomic number between the matrix atom and the substitute atom replacing it. Therefore, *Ga(PBi)* would give a more accurate composition determination than *Ga(AsBi)*, whilst *Ga(AsSb)* would be less accurate. For thickness determination, it would be the other way around. For *Ga(PBi)* the thickness determination is expected to perform worse than for *Ga(AsBi)*, while *Ga(AsSb)* is expected to yield more accurate results.

The concentration itself is also influencing the accuracy of composition determination and therefore also the accuracy of the proposed method. If the amount of both the substitute and the matrix atom is equal, i.e. a concentration of 50%, the number of possible arrangements of these atoms within an atomic column is highest. Therefore, the statistically determined composition determination performs worst for this concentration and this also converts to the proposed method.

However, these material system and concentration considerations are only of a theoretical nature since most of the time the material system to investigate is technologically dictated. Hence, the only remaining “free parameter” is the specimen thickness that is measured at. Then, the optimum thickness becomes a matter of specimen preparation and in particular the amorphous layers emerging during it.

The best detector range for simultaneous thickness and composition determination is determined by the potential to detect both the matrix and the substitute atom.

Generally, atoms with higher atomic number scatter electrons to higher angular ranges while atoms with lower atomic number like N mostly scatter to a lower angular range [32]. Since the total atomic number of one atomic column increases with thickness the best detector range for composition determination also depends on thickness. This was also found for atom counting [46]. A detailed analysis of the best imaging conditions for composition determination will be done in future work. For now, it is stated that the choice of the detection range is highly influential and offers great potential for future optimization and application.

The experimental results that were obtained considering the optimized angular range and thickness for STEM measurements are in very good agreement with the HR-XRD results. For these HR-XRD results, it has to be considered that HR-XRD yields only box-like concentration profiles that do not reflect the real concentration profile due to non-abrupt interfaces and non-constant concentration within the QW. Taking this into account, the composition profiles obtained by STEM investigations give a more detailed description even in 2D and furthermore, closely resemble the concentration profile assumed for HR-XRD.

The 2D composition map also reveals clustering effects for *Bi* atoms in *Ga(AsBi)* that have also been found before [8] and can be confirmed for this sample by considering the absolute atomic numbers for the composition.

Negative composition values for an atomic column are allowed with the purpose of taking into account the experimental noise present in the STEM image that will lead to intensity values that would belong to these negative compositions. Not allowing these negative compositions would bias the average concentration of one lattice plane to higher concentrations which is especially important for binary material where the average concentration of the substitute atom should be zero.

Locally, the experimental noise causes composition values of -1 *Bi* atoms and therefore gives a good estimation of the loss of accuracy that must be considered in addition to the inherent accuracy of the method of ± 1 *Bi* atoms for the given material system, composition and thickness.

The magnitude of experimental noise for a lattice plane can be detected within the binary material. Here, the standard deviation of the concentration within one lattice plane can be solely attributed to experimental noise since there are no composition fluctuations in binary material. In contrast, the higher standard deviations of concentration within one lattice plane within the *Ga(AsBi)*-QW is a combination of experimental noise and real composition fluctuations that are further increased by the clustering effects detected.

Non-zero average concentrations of the substitute atom within the binary matrix have been attributed to the presence of amorphous layers before [33]. There, the concentration of the substitute atoms for specimens prepared by conventional sample preparation and final treatment with a precision ion polishing system with an ion energy of 1.2 kV was substantially higher than 1%. Here, improved specimen preparation by using the NanoMill® TEM specimen preparation system with ion energies of 900 V could decrease the non-zero concentration as the *Bi* concentration detected in the *GaAs* barrier is -0.4%. This supports the argument that indeed the amorphous layers due to specimen preparation are responsible for non-zero concentrations of the substitute atom in the binary region. Hence, it is expected that further improvement of specimen preparation, i.e. the use of even lower ion energy and the reduction of the amorphous layers will bring the concentration of the substitute atom even closer to zero.

9. Summary

We showed a method to determine the thickness and composition of ternary III-V semiconductors on an atomic scale while aiming for single-atom accuracy. The statistical character of the experimental method allows this single-atom accuracy only for a certain fraction of atomic columns but looking at a high number of atomic columns an accurate overall composition determination is possible. In a simulation study, a proof of principle was given and the best detector range for image acquisition as well as limiting specimen thickness were investigated. When applying the method to an experimental STEM image excellent agreement with HR-XRD composition measurements was found.

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Figure Captions

Table 1: Parameters for STEM image simulations as determined for the microscope at hand

Fig. 1: Relationship between group V Voronoi intensity and *Bi* composition (a) and group III Voronoi intensity and average NN *Bi* composition (b) for *GaAsBi* at a total thickness of 30 atoms per atomic column. For both cases, all events within the simulated super cell (blue) are shown together with the mean intensity (red).

Fig. 2: (a) Simulated STEM image of *GaAsBi* containing 6% Bi at a thickness of 30 atoms per atomic column. (b) Thickness of group V atomic column determined initially via the group III sub lattice and comparison of Voronoi intensities to simulations. (c) Bi composition determined at the thicknesses shown in (b) by comparing to intensity composition relationships. (d) Deviation of determined composition shown in (c) to the real composition of the super cell. When comparing

STEM image in (a) and column representations in (b)-(d) note that only group V atomic columns are shown and edge regions of the image are excluded.

Fig. 3: Thickness (a), Bi composition (b) and deviation to the real composition (c) for the same simulated STEM image shown in 2(a) after applying the proposed method for thickness and composition determination with 5 cycles.

Fig. 4: STEM image of $(Ga_{0.7}In_{0.3})As$ for a thickness of 35 atoms per atomic column (a), together with the thickness (b), the composition (c) and the deviation to the real composition (d) determined by applying the proposed method. When comparing STEM image in (a) and column representations in (b)-(d) note that only group III atomic columns are shown and edge regions of the image are excluded.

Fig. 5: Detector angle dependency of the proposed method for a super cell of $Ga(AsBi)$ with 6 % Bi and a thickness of 30 atoms (a). Thickness dependency of the proposed method for the same super cell (b). In a simulation study, the deviation of the total Bi composition determined to the real composition of the super cell (black) and the fraction of group V atomic columns for which the composition (red) and the thickness (blue) were determined correctly were analysed.

Fig. 6: Application of the proposed method to an STEM image of a GaAsBi-QW grown by MOVPE. The STEM image (a) shows the GaAsBi-QW on the left and GaAs barrier on the right. Thickness map (b) after 15 iterative cycles. Composition map (c) for thicknesses shown in (b). The QW is clearly distinguishable. Concentration profile (d) of the initial (blue) and final (red) composition determination together with its standard deviation within one lattice plane (shaded red). For comparison reasons, also the concentration profile as determined by HR-XRD (black) is shown.

a

b

c

d