Electron channelling: challenges and opportunities for compositional analysis of nanowires by TEM

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Abstract

Energy dispersive x-ray spectroscopy in a transmission electron microscope is often the first method employed to characterize the composition of nanowires. Ideally, it should be accurate and sensitive down to fractions of an atomic percent, and quantification results are often reported as such. However, one can often get substantial errors in accuracy even though the precision is high: for nanowires it is common for the quantified V/III atomic ratios to differ noticeably from 1. Here we analyse the origin of this systematic error in accuracy for quantification of the composition of III–V nanowires. By varying the electron illumination direction, we find electron channelling to be the primary cause, being responsible for errors in quantified V/III atomic ratio of 50%. Knowing the source of the systematic errors is required for applying appropriate corrections. Lastly, we show how channelling effects can provide information on the crystallographic position of dopants.

Keywords: III-V semiconductor, nanowire, electron microscopy, EDS, ternary

(Some figures may appear in colour only in the online journal)

1. Introduction

Energy dispersive x-ray spectroscopy (EDS) has become the standard transmission electron microscopy (TEM) technique for characterizing the chemical makeup of nanowires [1]. The wide use of EDS is due to its ease of use combined with high spatial resolution (commonly on the nanometre scale, but ultimately down to individual atomic columns [2]), and nominal high accuracies and sensitivities (commonly in the low tenths of atomic\%, but ultimately down to just a few atoms [3]). Notable examples of uses of EDS for nanowires include: assessing the composition of ternary and quaternary III–V compounds [4–7], compositional profiling in heterostructures [8–13], assessing doping levels and dopant profiling [14], and measuring seed particle composition [15–17]. However, for III–V nanowires it is not uncommon to see up to 50% deviations from the expected V/III atomic ratio of 1. Such large deviations in stoichiometry are inconsistent with the phase behaviour of III–V materials—and with the excellent crystal qualities and electronic properties reported for nanowires—and must therefore be the result of systematic errors in the EDS measurements and quantifications.

Finding the source of the quantification errors is necessary in order to apply corrections and understand the limitations of quantitative EDS when applied to nanowires. Due to these errors, quantified V/III atomic ratios are currently rarely reported for nanowires. Instead it is common, in the case of ternary compounds, to use only the ratios between the measured group V or group III contents. A measured composition of, for example, In\textsubscript{0.4}As\textsubscript{0.2}P\textsubscript{0.4} is thereby converted to InAs\textsubscript{0.33}P\textsubscript{0.67}. However, without knowing the source of the error in the original quantification, we cannot know if this simple conversion
scheme is warranted. Potentially, the same systematic errors that skew the measured V/III ratio also skew the V/V or III/III ratios, which would be highly problematic for all analyses and conclusions based thereon. Here, we analyse the origin of the systematic EDS errors by varying illumination conditions and illumination time while recording the spectra. We investigate both InP and GaAs nanowires as examples of III–V materials with dissimilar and similar III and V atomic numbers, respectively. We find electron channelling along the different atomic columns to be the dominant cause of quantification errors, being responsible in this case for differences of up to 10 atomic percentage points. The other sources of errors investigated—surface oxidation and alteration by the electron beam—can at most account for differences of 1 atomic percentage point. In light of this we suggest best practices for accounting for the channelling effects and avoid confusion of when/how to normalize the estimated compositions. Electron channelling is however not only a source of quantification errors, but could also provide unique opportunities for separating the compositions of different sublattices in the crystal [18]. We therefore also include an outline of how this effect can provide information on dopant location in III–V materials.

2. Experimental details

The nanowire samples used for the present study were grown by metal organic vapour phase epitaxy (MOVPE) following the vapour-liquid-solid growth mechanism. InP nanowires were seeded by Au particles and grown at a set temperature of 420 °C, a reactor pressure of 100 mbar, and a total carrier gas flow of 6 slm. At a PH₃ molar fraction of χ(Ph₃) = 1.85 × 10⁻² the 111B-oriented, epiready substrate was annealed for 10 min at a set temperature of 600 °C to desorb residual surface oxides. An initial nanowire growth step of 60 s was initiated at 420 °C by lowering the supply of PH₃ to χ(Ph₃) = 6.2 × 10⁻³ and introducing trimethylindium (TMIn) at a molar fraction of χ(TMIn) = 9.5 × 10⁻⁶. After that nucleation step 50 min of InP:S growth followed by additionally introducing H₂S at a molar fraction of χ(H₂S) = 1.25 × 10⁻⁴. Nanowire growth was terminated by turning of the TMIn and H₂S sources simultaneously and cooling the sample under PH₃ to 300 °C.

In the case of the GaAs:Sn nanowires, Sn was used as foreign seeding agent to initiate nanowire growth on an 111B-oriented GaAs wafer piece at a set temperature of 500 °C, a reactor pressure of 100 mbar, and a total carrier gas flow of 13 slm. An annealing step was carried out for 10 min at a set temperature of 630 °C at an AsH₃ molar fraction of χ(AsH₃) = 1.5 × 10⁻³. After setting the temperature to 550 °C Sn particles were formed in situ by supplying tetraethyltin (TESn) at a molar fraction of χ(TESn) = 1.2 × 10⁻⁵ at a lower AsH₃ molar fraction of χ(AsH₃) = 3.6 × 10⁻⁵ for 15 min. The GaAs nanowire growth was carried out for 10 min at 500 °C by supplying trimethylgallium (TMGa) at a molar fraction of χ(TMGa) = 9.1 × 10⁻⁵ and AsH₃ at χ(AsH₃) = 7.7 × 10⁻⁵ before terminating growth by closing the TMGa supply and cooling the sample under the set AsH₃ flow to 300 °C [19].

TEM characterization was performed using a JEOL 3000 F transmission electron microscope operated at 300 kV and equipped with an Oxford Instruments X-Max silicon drift detector for EDS. Samples were prepared for TEM by gently pressing lacy carbon coated copper grids to the growth substrates. In this process, nanowires were broken off at random (in terms of position and height on the substrate) and transferred with random orientations, although with a tendency to lie flat, onto the lacy carbon film. X-ray spectra were acquired over a 60 s live time using a close to parallel electron beam (0.2 mrad convergence semi-angle estimated from diffraction patterns), approximately 200 nm in diameter at an electron dose rate of ca. 2000 e⁻/(s × nm²). Quantification was performed using the Inca software package (Oxford Instruments), which utilizes the Cliff-Lorimer technique with correction routines for detector efficiency, absorption and fluorescence. For each nanowire being analysed, mechanical tilt was used to orient the crystal to within a few tenths of a degree to a [112] or [1100] zone axis perpendicular to the growth direction for zinc blende and wurtzite nanowires, respectively. Beam tilt was used for the final alignment to the zone axis, based on Kikuchi lines, in order to achieve a precision of a few mrad. Beam tilt was also used to select Bragg conditions for specific planes in the zone in subsequent measurements. Beam location along the nanowire and diffraction conditions were evaluated before and after each x-ray spectrum acquisition to ensure that no significant sample drift or tilt occurred over the measurements.

Orientation dependent ionization cross sections were simulated using ICSC (v. 1.2) [20], utilizing a Bloch wave model (91 diffracted beams included) for calculating the electron distribution in the sample, and parametrized inelastic cross sections [21] to account for delocalization of the ionization interaction. Thermal diffuse scattering (TDS) was included using Debye-Waller factors (300 K, from reference [22]), with TDS electrons approximated as a plane wave. Mass-weighted thickness was used to select thicknesses for the simulations (150 nm for InP and 80 nm for GaAs). Simulations were carried out for wurtzite InP along [1100] and for zinc blende GaAs along [112].

3. Results and discussion

3.1. The source of error in EDS quantification

The systematic errors in EDS quantification can result in a wide range of apparent deviations from stoichiometry: in the present paper we will show examples of both high measured V/III atomic ratios (e.g. In₀.₄₁P₀.₅₉) and low ratios (e.g. Ga₀.₅₄A₀.₄₆). It is important to note from the start that these skewed V/III ratios are not due to an erroneous correction of x-ray absorption and fluorescence in the quantification routine; no setting of the two parameters used for this correction (sample thickness and density) will consistently result in stoichiometric compositions.

There are three main possible sources for the systematic errors: oxidation of the nanowire surfaces, alterations of the nanowire induced by the electron beam, or electron channelling effects. Oxidation during transfer from growth...
chamber to electron microscope will always occur to some extent and could lead to selective loss of one element from the nanowire surface [23]. Likewise, it is difficult to completely avoid alterations by the electron beam while observing the sample (or indeed, while recording x-ray spectra) in the electron microscope—potentially impacting one constituent element more through atomic-number dependent damage mechanisms [24]. Channelling effects are related to the dynamical diffraction of the incoming electron beam into a standing wave inside the illuminated crystal; the electron intensity thereby increases and decreases periodically along the different atomic columns in a manner that is highly sensitive to the exact diffraction condition [18]. This effectively breaks the fundamental assumption in EDS quantification that the electron beam is evenly distributed through the sample and thus generates x-rays from the constituent elements in proportion to their overall abundance. These three effects each have different implications for how the obvious errors in measured V/III ratios might translate to errors in ratios between different V or III elements in ternary materials, or to the concentration of minority elements (e.g. dopants). They each also are affected differently by operator choices in sample preparation and EDS recording setup, which allow us to separate their effects.

Electron channelling always occurs to some extent in thin crystalline samples, but the effect becomes particularly strong close to low-index zone axes where atoms in projection line up into well-separated columns [18]. This is a very common situation for nanowires which are often imaged and analysed in a direction which is perpendicular to their growth axis, either by design (i.e. in order to measure the composition of different sections along the length of the nanowire) or simply because they have a tendency to lie flat on the TEM grid. For the common [111] growth direction of zinc blende nanowires, this orients the (111) and (111) planes exclusively containing III and V atoms, respectively, parallel to the electron beam. For wurtzite nanowires the situation is the same, with corresponding growth direction [0001] and planes (0002) and (0002) when indexed using the hexagonal notation. If the electrons preferentially channel along, e.g. the (111) planes an artificially high III content will be measured. Note that separation of III and V atoms to different columns in projection is not an absolute requirement for channelling to result in differences in x-ray generation [18].

Probing electron channelling by recording x-ray spectra at different diffraction geometries reveals a large effect. As illustrated for an InP nanowire in figure 1(a), we start from an on-zone [1100] orientation as (1) it is a common situation for nanowire analysis and (2) it simplifies comparison between samples as the zinc blende and wurtzite crystal structure types are identical in this projection. For consistency, all illustrations and images are presented with the nanowire growth direction from left to right. From this starting point we tilt or rotate the electron beam with respect to the nanowire as illustrated in figure 1(b), collecting x-ray spectra at each orientation. The magnitude of the tilts and rotations are measured from the shift of the diffraction pattern as shown by the comparison of figures 1(c) and (d). The corresponding spectra, shown in figure 1(e), have noticeable differences in ratio between the In- and P-associated peaks and consequently result in different V/III ratio after quantification.

Electron channelling can account for very large variations in quantification results. These variations are summarized in figure 2, where the apparent composition is plotted against the tilt/rotation away from the initial on-zone orientation. For InP (figure 2(a)), tilting the beam in either direction results in large excess intensity for the P-related peaks in the spectra. As expected due to the non-centrosymmetric nature of the wurtzite (and zinc blende) structure, the response is not symmetric around the on-zone orientation; setting the In-containing (0002) plane (or multiples thereof) at Bragg condition yield a larger excess of P than tilts in the opposite direction. For GaAs (figure 2(b)), setting the Ga-containing (111) planes (and multiples thereof) at Bragg condition result in measured V/III atomic ratios higher than 1, while tilts in the
other direction yield V/III ratios lower than 1. Rotation of the electron beam around the nanowire growth axis results in comparatively small changes, as shown in figure 2(c) for InP. This is consistent with rotation primarily shifting electron intensity between (1120) and (1120) planes with identical, stoichiometric InP compositions.

Simulations of orientation dependent ionization cross sections, included in figure 2, confirm the role of electron channelling in generating the erroneous quantifications. In order to display the simulation and quantification results in the same graph, we use ratios between the relevant cross sections (P-K and In-L, and As-K and Ga-K ionization, respectively) and normalize these to effective ‘k-factors’ that replicate the experimental on-zone results. This assumes that the remaining factors determining the x-ray signal (fluorescence yield, x-ray absorption, effective detector solid angle, and detector efficiency [25]) are constant, which is reasonable given that the beam tilt only varies by a few mrad. While the excesses and deficiencies are more pronounced in the simulations, the resulting V/III ratios follow the trends with tilt and rotation observed in the experiments well. We attribute the dampened variations in the experimental data to the EDS spectra being averaged for several different thicknesses, and the tilts and rotations changing slightly while recording the spectra (in contrast to the single thickness and perfectly defined orientation of the simulation) [20]. Through the comparisons with the simulations, it becomes possible to assign growth-direction polarity to [0001] and [111], i.e. with group V-terminated growth planes for the InP and GaAs nanowires presented here, respectively. While such EDS measurements and simulations are not difficult to perform [20], convergent beam electron diffraction [26] or, better yet, atomic-resolution imaging [27] and spectroscopies [28] can also provide this (and much more) information.

Channelling effects are not limited to the near-zone orientations analysed in figure 2, but remain even after several degrees of tilt and rotation. For InP, we measure compositions corresponding to In$_{0.54}$P$_{0.46}$ after 6° rotation and In$_{0.48}$P$_{0.52}$ after 10° tilt. Here, the sample itself is rotated/tilted rather than the electron beam, but the results remain consistent with the trends presented in figure 2. Converging the electron beam on the sample also has limited effect; the difference for InP is less than 1 percentage point between parallel and 5 mrad convergence semi-angle both on-zone and with (0004) at Bragg condition. Larger convergence angles (such as those used in aberration corrected scanning TEM (STEM)) will be better at evening out the channelling effect, but will not remove them completely [29, 30]. In particular, for InP most orientations result in an excess of P which is therefore unlikely to be averaged out at any convergence angle.

Electron beam induced alterations can only account for very minor errors in EDS quantification under the circumstances reported here. Going back to on-zone conditions repeatedly throughout the measurement series presented in figure 2, we see only a 1 percentage point difference developing over the course of 1 h of continuous irradiation. The electron dose accumulated between these measurements is of the order of $10^7$ e$^-\cdot$nm$^{-2}$. Note that the change in measured composition over time does not follow a clear trend; while the apparent P content increased over time for the on-zone measurement, it decreased by similar amounts for the repeated measurements with (0004) at Bragg condition. Small, unintentional differences in the diffraction conditions are enough to explain these variations. This is not to rule out the potential of electron beam induced changes—it is after all quite easy to ‘drill holes’ through thinner nanowires with a focused electron beam. However, these measurements do indicate that this mechanism cannot gradually build up large differences in composition without noticeable structural changes.
The formation of native oxides on III–V materials is a complex process, yielding a variety of different phases depending on the exact conditions [23]. From an EDS quantification point of view, the worst case scenario would be a complete loss of the more volatile group-V oxides, leaving behind e.g. Ga$_2$O$_3$ or In$_2$O$_3$. This mechanism would always lead to measured V/III ratio below 1 with the apparent reduction in group-V content strongly connected to the nanowire diameter. Assuming the formation of a 1 nm oxide layer in this fashion, the resulting overall composition will only be shifted to, for the sake of comparison with the nanowires presented here, In$_{0.51}$P$_{0.49}$ for a nanowire 100 nm in diameter. We note that the magnitude of this effect therefore should be much smaller than the variation caused by channelling.

3.2 Implications for composition of ternaries

To a first approximation, channelling should not cause any discrepancies for elements located on the same sub-lattice in the crystal since they will be exposed to the same electron intensity. This supports the common practice of using III/III or V/V ratios from EDS quantifications in the case of ternary materials. However, this ignores the fact that delocalization of the ionization interaction can differ between the constituent elements; low-energy characteristic x-rays can be generated by electrons further away from the atomic position than high-energy x-rays, leading to skewed ratios in the quantification.

Simulations of orientation dependent ionization cross sections for Al$_x$In$_{1-x}$P and Ga$_x$In$_{1-x}$P demonstrate that III/III ratios can vary by 10% for different diffraction conditions, as shown in figure 3(a). The simulations cover the same range of beam tilts as figure 2(a), but are based on a 40 nm thick InP crystal to reduce the influence from thermal diffuse scattering [25, 31]. Although there are variations in the apparent III/III ratio, it is much smaller than the simultaneous variation in apparent V/III ratio shown in figure 3(b). Note that there is no simple connection between the errors in the estimated III/III and V/III ratios.

The simulations in figure 3 indicate that III/III and V/V ratios in ternary III–V materials should be interpreted with some caution; the systematic error due to channelling effects is reduced but not completely mitigated. An exhaustive exploration of the magnitude of such quantification errors for different ternaries, compositions, and diffraction conditions is beyond the scope of this paper. If high accuracy is needed, detailed simulations should be undertaken for the specific conditions used. For STEM, it is possible to use such simulations to almost completely remove the effects of channelling, delocalization and thermal diffuse scattering to recover the absolute number of atoms of each element under the electron probe [30, 32, 33]. We note that nanowires could be ideal samples for such techniques in future studies given their often well-defined morphology, which allow for simple and accurate local thickness determination.

3.3 Implications for dopant concentrations

The effects discussed for ternary materials in the previous section applies equally to measurements of dopant concentrations. Some dopant elements however come with the additional complication that they can substitute both group III and group V atoms in the lattice. Here electron channelling can be useful by enabling measurements of the composition of the individual sub-lattices in the crystal: a technique known as ALCHEMI (Atom Location by Channelling Enhanced Microanalysis) [18, 34]. An outline of such an analysis is provided in figure 4, where the measured Sn-content in the GaAs nanowire is correlated to the measured Ga-fraction (see figure 2) and compared to simulations of the same. In the model, the in-principle amphoteric Sn is located entirely on the Ga sub-lattice. Because the channelling effect is larger than the effects of delocalization of the ionization interactions, there is a clear positive, linear correlation between the two in the simulation (albeit with some variations); when the electrons channel along the Ga columns, they encounter Sn substituents more often than when channelling along the As columns. The similar correlation for the experimentally measured Sn content indicates that its distribution is similar to the model’s. The location of Sn on the Ga sub-lattice is consistent with the previously reported exclusive n-doping electrical characteristics of the Sn-doped GaAs nanowires [35]. The comparison between the simulated and experimental Sn-Ga...
Figure 4. (a) Correlation of the measured Sn content in the GaAs:Sn nanowires to the measured Ga concentration. Both experimental results (●) and simulations (×), assuming 1.1 at% Sn located entirely on the Ga sub-lattice, are included. Due to differences in ionization interaction delocalization, the indicated Sn and Ga concentrations are not perfectly correlated even in the simulations. A linear regression is included for the simulated results. The spectra from the two extreme cases of low-Ga-low-Sn and high-Ga-high-Sn are shown in (b).

correlation is, however, limited by the low counting statistics for the Sn signal in the latter. This shortfall should be addressed for future analyses to generate more reliable and definite results.

Imaging [36, 37] and atomic-column resolved spectroscopy [38] provide alternative techniques for locating dopant atoms. The overall, statistical picture provided by ALCHEMI might however complement such measurements, which can only reasonably pin-point the location of a few example dopant atoms at a time.

4. Conclusion

The main conclusions regarding electron channelling in III–V nanowires can be summarized as follows:

- Electron channelling is the dominant cause for the apparent deviations from stoichiometry often measured for III–V nanowires by EDS—with possible exceptions for thin, visibly oxidized or damaged nanowires.
- The electron channelling effect is particularly severe for near zone-axis orientations and will be important for the full range of nanowire diameters commonly studied.
- Electron channelling primarily influences the measured ratios between elements on different sub-lattices, but differences in delocalization of the ionization interaction means that all measured concentrations are affected to some extent.
- ALCHEMI opens up the possibility of statistically locating minor elements, e.g. dopants, to III or V sites in the crystal.

We recommend the following for dealing with channelling effects in EDS analysis of nanowires:

- Ignore the deviations from V/III stoichiometry (but see caveats above)—correcting for channelling, including delocalization effects, will be more trouble than it is worth and any real deviations due to, e.g. vacancies will be too small to detect by EDS anyways.
- For ternaries, V/V and III/III ratios can be slightly skewed by electron channelling effects. If accuracies better than about 10% are crucial, comparison with simulations are required. For reporting general trends in composition with e.g. growth conditions, uncorrected ratios are however sufficient.
- For minor elements there are three options: (1) report quantification results as received together with the apparent V/III ratio, (2) normalize the quantification based on their assumed location on either III or V sites, or (3) conduct a full ALCHEMI analysis.

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References

[1] Zamani R R and Arbiol J 2019 Understanding semiconductor nanostructures via advanced electron microscopy and spectroscopy Nanotechnology 30 262001
[2] D’Alfonso A J, Freitag B, Klenov D and Allen L J 2010 Atomic-resolution chemical mapping using energy-dispersive x-ray spectroscopy Phys. Rev. B 81 100101(R)
[3] Watanabe M, Ackland D W, Burrows A, Kiely C J, Williams D B, Krivanek O L, Delhys N, Murfitt M F and Szilagyi Z 2006 Improvements in the X-ray analytical capabilities of a scanning transmission electron microscope by spherical-aberration correction Microsc. Microanal. 12 515–26
[4] Heiss M et al 2013 Self-assembled quantum dots in a nanowire system for quantum photonics Nat. Mater. 12 439–44
[5] Kauko H, Grieb T, Bjørge R, Schwalzer M, Munshi A M, Weiman H, Rosenauer A and van Helvoort A T J 2013 Compositional characterization of GaAs/GaAsSb nanowires by quantitative HAADF-STEM Micron 44 254–60
[6] Wallentin J, Persson J M, Wagner J B, Samuelson L, Deppert K and Borgström M T 2010 High-performance single nanowire tunnel diodes Nano Lett. 10 974–9

[7] Tizzi L, H G, Chiaramonte T, Ugarte D and Cotta M A 2009 III-V semiconductor nanowire growth: does arsenic diffuse through the metal nanoparticle catalyst? Nanotechnology 20 275804

[8] Krogstrup P, Yamasaki J, Sørensen C B, Johnson E, Wagner J B, Pennington R, Aagesen M, Tanaka N and Nygård J 2009 Functions in axial III-V heterostructure nanowires obtained via an interchange of group III elements Nano Lett. 9 3689–93

[9] Wen C-Y, Reuter M C, Bruley J, Tersoff J, Kodambaka S, Stach E A and Ross F M 2009 Formation of compositionally abrupt axial heterojunctions in silicon-germanium nanowires Science 326 1247–50

[10] Ek M, Borg B M, Johansson J and Dick K A 2013 Diameter limitation in growth of III-Sb-containing nanowire heterostructures ACS Nano 7 3668–75

[11] Paladugu M, Zou J, Guo Y-N, Auchtelonie G J, Joyce H J, Gao Q, Tan H H, Jagadish C and Kim Y 2007 Novel growth phenomena observed in axial InAs/GaAs nanowire heterostructures Small 3 1873–7

[12] Gadiksen M S, Lauhon L J, Wang J, Smith D C and Lieber C M 2002 Growth of nanowire superlattice structures for nanoscale photonics and electronics Nature 415 617–20

[13] Hocevar M, Immink G, Verheijen M, Akopian N, Zwiller V, Kouvonenhoen L and Bakkers E P A M 2012 Growth and optical properties of axial hybrid III-V/Silicon nanowires Nat. Commun. 3 1266

[14] Wallentin J, Mergenthaler K, Ek M, Wallenberg L R R, Samuelson L, Deppert K, Pistol M-E and Borgström M T 2011 Probing the Wurtzite conduction band structure using state filling in highly doped InP nanowires Nano Lett. 11 2286–90

[15] Zannier V, Ercolani D, Gomes U P, David J, Gemmi M, Dubrovskii V G and Sorba L 2016 Catalyst composition tuning: the key for the growth of straight axial nanowire heterostructures with group III interchange Nano Lett. 16 7183–90

[16] Ek M, Borg B M, Dey A W, Gnanipour B, Thelander C, Wernersson L-E and Dick K A 2011 Formation of the axial heterojunction in GaSb/InAs(Sb) nanowires with high crystal quality Cryst. Growth Des. 11 4588–93

[17] Wang J, Pfüssel S R, Verheijen M A, Feiner L-F, Cavalli A and Bakkers E P A M 2013 Reversible switching of InP nanowire growth direction by catalyst engineering Nano Lett. 13 3802–6

[18] Jones I P 2003 Determining the locations of chemical species in ordered compounds: ALCHEMI Advances in Imaging and Electron Physics ed P W Hawkes (New York: Academic) Vol 125 pp 63–117

[19] Sun R, Vainorius N, Jacobsson D, Pistol M E, Lehmann S and Dick K A 2016 Sn-seeded GaAs nanowires grown by MOVPE Nanotechnology 27

[20] Oxley M P and Allen L J 2003 ICSCC: A program for calculating inelastic scattering cross sections for fast electrons incident on crystals J. Appl. Crystallogr. 36 940–3

[21] Oxley M P and Allen L J 2000 Atomic scattering factors for K-shell and L-shell ionization by fast electrons research papers Acta Crystallogr. A 56 470–90

[22] Reid J S 1983 Debye–Waller factors of zinc-blende-structure materials – a lattice dynamical comparison Acta Crystallogr. A 39 1–13

[23] Wilmansen C W 1981 Chemical composition and formation of thermal and anodic oxide/III-V compound semiconductor interfaces J. Vac. Sci. Technol. 19 279–89

[24] Egerton R F, Li P and Malac M 2004 Radiation damage in the TEM and SEM Micron 35 399–409

[25] Chen Z, D’Alfonso A J, Weyland M, Taplin D J, Allen L J and Findlay S D 2015 Energy dispersive X-ray analysis on an absolute scale in scanning transmission electron microscopy Ultramicroscopy 157 21–26

[26] Lehmann S, Wallentin J, Märtensson E K, Ek M, Deppert K, Dick K A and Borgström M T 2019 Simultaneous growth of pure Wurtzite and zinc blende nanowires Nano Lett. 19 2723–30

[27] de la Mata M et al 2012 Polarity assignment in ZnTe, GaAs, ZnO, and GaN–AlN nanowires from direct dumbbell analysis Nano Lett. 12 2579–86

[28] Zamani R R, Hage F S, Lehmann S, Ramasse Q M and Dick K A 2018 Atomic-resolution spectrum imaging of semiconductor nanowires Nano Lett. 18 1557–63

[29] Liao Y and Marks L D 2013 Reduction of electron channeling in EDS using precession Ultramicroscopy 126 19–22

[30] Chen Z, Weyland M, Sang X, Xu W, Dycus J H, LeBeau J M, D’Alfonso A J, Allen L J and Findlay S D 2016 Quantitative atomic resolution elemental mapping via absolute-scale energy dispersive X-ray spectroscopy Ultramicroscopy 168 7–16

[31] Forbes B D, Alfonso A J D, Williams R E A, Srinivasan R, Fraser H L, Mccomb D W, Freitag B, Klenov D O and Allen L J 2012 Contribution of thermally scattered electrons to atomic resolution elemental maps Phys. Rev. B 86 024108

[32] Lugg N R, Neish M J, Findlay S D and Allen L J 2014 Practical aspects of removing the effects of elastic and thermal diffuse scattering from spectroscopic data for single crystals Microsc. Microanal. 20 1078–89

[33] Macarthur K E, Brown H G, Findlay S D and Allen L J 2017 Probing the effect of electron channelling on atomic resolution energy dispersive X-ray quantification Ultramicroscopy 182 264–75

[34] Spence J C H and Taito J 1983 ALCHEMI: a new technique for locating atoms in small crystals J. Microsc. 130 147–54

[35] Sun R, Jacobsson D, Chen J-J, Nilsson M, Thelander C, Lehmann S and Dick K A 2015 Sn-seeded GaAs nanowires as self-assembled radial p-n junctions Nano Lett. 15 3757–62

[36] Allen J E et al 2008 High-resolution detection of Au catalyst atoms in Si nanowires Nat. Nanotechnol. 3 168–73

[37] Bar-Sadan M, Barthel J, Shtrikman H and Houben L 2012 Direct imaging of single Au atoms within GaAs nanowires Nano Lett. 12 2352–6

[38] Geaney H, Mullane E, Ramasse Q M and Ryan K M 2013 Atomically abrupt silicon-germanium axial heterostructure nanowires synthesized in a solvent vapor growth system Nano Lett. 13 1675–80