Polarity Assignment in ZnTe, GaAs, ZnO, and GaN-AlN Nanowires from Direct Dumbbell Analysis

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Supporting Information

ABSTRACT: Aberration corrected scanning transmission electron microscopy (STEM) with high angle annular dark field (HAADF) imaging and the newly developed annular bright field (ABF) imaging are used to define a new guideline for the polarity determination of semiconductor nanowires (NWs) from binary compounds in two extreme cases: (i) when the dumbbell is formed with atoms of similar mass (GaAs) and (ii) in the case where one of the atoms is extremely light (N or O: ZnO and GaN/AlN). The theoretical fundamentals of these procedures allow us to overcome the main challenge in the identification of dumbbell polarity. It resides in the separation and identification of the constituent atoms in the dumbbells. The proposed experimental via opens new routes for the fine characterization of nanostructures, e.g., in electronic and optoelectronic fields, where the polarity is crucial for the understanding of their physical properties (optical and electronic) as well as their growth mechanisms.

KEYWORDS: Dumbbell, polarity, annular bright field, ABF, high angle annular dark field, HAADF, scanning transmission electron microscopy, STEM, semiconductor nanowires

The existence of internal electric fields in ionic crystals has a straightforward impact on many physical properties that determine the electronic structure, the local charge carrier distribution and the related electromagnetic features, among others.1 The polarity in compound semiconductors arises from the partial ionicity of their chemical bonds. The charge transfer between the elements of the compound results in the formation of atomic pairs of opposite partial charge (ionicity), which are commonly referred to as “dumbbells”. The oppositely signed charge of the atoms constituting the dumbbells implies the existence of this internal electric field in the crystal.1 In nanoscale structures such as nanowires (NWs), it turns out that only a particular polarity drives the unidirectional growth.2–5 Indeed, as it has been demonstrated recently, it influences the growth mechanism, drives the final orientation of the nanowires2,6 or can even lead to the formation of new nanostructures such as tripods.7 Polarity driven growth...
mechanisms can even explain the formation of kinking in some semiconductor heterostructures. Nevertheless, in spite of this advancement in the role played by the polarity in the nanostructures growth mechanisms, there is also an important issue regarding the conservation of polarity along the nanostructure, and particularly through the twin boundaries that needs to be addressed. Twins correspond to 180° rotations of the structure along the [111] or [0001] growth axes in zinc-blende (ZB) or wurtzite (WZ) structure, respectively. Orthotwins correspond to twin defects where the polarity is conserved across the boundary, while in paratwins it is not. It is not yet clear what happens at the nanostructure level due to the intrinsic difficulties to determine it.

Reliable methods for polarity determination of compound semiconductor NWs at the atomic scale are still scarce, although several approaches have been reported, lacking spatial resolution. The simplest method, which is not sensitive down to the atomic scale, is the homoepitaxy of the NWs on a substrate. Here, one assumes that the polarity is conserved at the interface and that the orientation of the nanowire corresponds with that defined for the substrate. In addition to the nonuniversality of this method because it cannot be applied for the growth on nonpolar or amorphous substrates, it also opens the question of polarity conservation at the interface and also in the formation of inversion boundaries on the substrate. Here, one assumes that the polarity is conserved at the interface and that the orientation of the nanowire corresponds with that defined for the substrate. In addition to the nonuniversality of this method because it cannot be applied for the growth on nonpolar or amorphous substrates, it also opens the question of polarity conservation at the interface and also in the formation of inversion boundaries on the substrate. Here, one assumes that the polarity is conserved at the interface and that the orientation of the nanowire corresponds with that defined for the substrate.

While the second method is limited to the cleavage planes of the sample, the first method requires the removal of the first surface monolayers in order to leave a clean surface which can often damage the structure. Another common used technique is the convergent beam electron diffraction (CBED). Here, the CBED patterns are compared with simulated images of different polarity. Although this is an established methodology, especially in thin films, it has several drawbacks that limit its use in the case of nanostructures and might cause misleading results: first, due to the large volume needed for accurate diffraction, samples with extremely small diameter cannot be easily investigated. Second, it has a low spatial resolution, which as a consequence does not allow the visualization of polarity changes at an interface, such as at an antiphase boundary (APB). Finally, the technique becomes highly challenging in cases where the NW exhibits a high density of twins or even twins occurring in the three-dimensional space. Another technique that offers the possibility of obtaining compositional information at the atomic scale is the scanning tunneling microscopy (STM). STM is also a constrained technique which cannot be applied to all structures. Nanowires can be investigated in two configurations only: (i) by directly positioning them on a conductive substrate or (ii) by embedding them in a matrix and cleaving the substrate in situ in the microscope. While the second method is limited to the cleavage planes of the sample, the first method requires the removal of the first surface monolayers in order to leave a clean surface which can often damage the structure. In addition, the spatial resolution is often not good enough to distinguish both atoms in the dumbbell, which are typically separated by only 0.11–0.15 nm (see Table 1). Furthermore, the visualization of light elements (e.g., O and N), which are main components in many compound semiconductors like metal oxides or nitrides is not possible.

The ability to determine the polarity across hexagonal/cubic (2H/3C) faulted structures at atomic resolution was first reported in GaN by means of HRTEM. Later on, the polarity of ZnO from direct structural images was also reported. Dumbbell images from single atomic layers of BN with Z differences as small as 2 were also reported and interpreted elsewhere.

Also by means of HRTEM, many physical properties such as a polar ordering in GeTe are nowadays directly extracted from dumbbell images of nanostructures. However, although HRTEM has been demonstrated to be a powerful tool for achieving the top spatial resolutions, it has been always applied to nanostructured systems with low thicknesses (few nanometers). In the precedent cases, only atomically flat sample wedges, thin nanoparticles or exfoliated ultrathin layers could be analyzed, sometimes requiring an additional computer simulation process to recognize the patterns or either reconstruct the images.

### Table 1. Atomic Distances between Constituent Atoms of Dumbbell Pairs along the [110]_{ZB} or [11−20]_{WZ} Projections for ZnTe (ZB), GaAs (ZB), ZnO (WZ), GaN (WZ), and AlN (WZ), where ZB Refers to the Zinc-Blende Cubic Structure and WZ to the Wurtzite Hexagonal Structure

<table>
<thead>
<tr>
<th>Material</th>
<th>Atomic Distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTe</td>
<td>0.152</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.141</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.115</td>
</tr>
<tr>
<td>GaN</td>
<td>0.109</td>
</tr>
<tr>
<td>AlN</td>
<td>0.109</td>
</tr>
</tbody>
</table>

Other techniques with a high spatial resolution and a chemical contrast (sensitivity) include spectrum imaging (SI) by electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDX), both performed in a scanning transmission electron microscope (STEM). While atomic resolution in EELS was already accomplished in the 90s, and with more chemical accuracy during the past decade, the case of EDX it has just recently been demonstrated. The drawback here is that it necessitates a long acquisition time and intense electron beams that often result in the degradation of the material as well as a long postobservation data processing.

All of these difficulties and limitations have contributed to the fact that up to now, reliable methods are not yet operative and polarity data with atomic resolution for many samples is not available (e.g., raw nanowires).

In contrast, as we report in this paper, there is a better approach for determining the polarity in semiconductor nanowires; the aberration corrected scanning transmission electron microscopy (STEM) which can reach direct imaging at sub-Angstrom resolution. This is an advantageous approach with respect to the above-mentioned requirements, additionally benefiting from straightforward sample preparation in the case of NWs, which are mechanically removed from the substrate, transferred to a holey or lacey carbon grid and placed in the microscope (no need of extra sample preparation to achieve atomically flat wedges). We distinguish between three different cases of compound semiconductors, according to the atomic number (Z) of the dumbbell constituents, for which the technique has to be applied in a different manner: i) high-medium Z (such as in ZnTe); ii) nearly identical Z (GaAs); and iii) low Z (GaN and ZnO). All images presented here were obtained in STEM mode, although they were acquired using different methodologies. For the first two systems we provide high angle annular dark field (HAADF) images, while for the last two, involving lighter elements, we present a novel methodology based on annular bright field (ABF) STEM imaging for the determination of the local polarity with atomic resolution. Finally, we will present theoretical calculations of the conductivity in the ballistic regime, showing that the change of polarity in a twin perpendicular to the growth axis in a GaAs NW can dramatically decrease the carrier transport within the
nanowire, due to scattering at the polar twin boundary. This work opens the route for the investigation of polarity in compound semiconductors in a reliable and rapid manner, thereby enabling a direct correlation with the functional properties and enhanced understanding of the related growth mechanisms.

**HIGH-MEDIUM ATOMIC NUMBER**

Figure 1 presents polarity imaging in ZnTe NWs using two different STEM methods. The first one corresponds to HAADF or Z-contrast imaging. As shown in the inset of Figure 1A, the images are obtained by scanning the electron beam across the sample and collecting the electrons scattered elastically at high angles, mainly due to interactions with phonons (thermal diffuse scattering or TDS), resulting in incoherent imaging with chemical contrast. The resulting images are intuitively interpretable atomic resolution images where the observed contrast scales with the atomic number (Z) of the atomic columns. In this way, it is possible to resolve atomic columns within the dumbbell and to identify the different elements as a consequence of the Z dependence (as it is the case for ZnTe). Nevertheless, the Z contrast makes the lightest elements almost undetectable when combined with heavier atoms.

The second method is ABF STEM, which has recently been used successfully for the imaging of the lightest elements such as hydrogen. In this case, the required setup consists of a bright field detector in which the central area is covered with a beam stopper or, equivalently, an annular detector that collects the direct beam diffraction disk (top right inset in Figure 1C). With this setup, the image is formed from the wave interference of the elastically scattered electrons, with negligible contribution from TDS (particularly for light elements). The resulting phase image allows the visualization of light and heavy atomic columns which will be of special interest in the case of O and N atomic columns in ZnO and GaN/AlN compounds (see the Supporting Information for more details on the experimental setup and properties of both techniques, S1 and S2).

We first demonstrate both techniques for the case of ZnTe NWs, composed by heavy elements with clearly differentiated Z, an element of high atomic number (Z > 50) and another element with midvalued atomic number (50 > Z > 15), i.e., the so-called “high-medium atomic number” compounds (Table S1). The ZnTe NWs were obtained by the vapor transport technique, with the layered-structured muscovite mica as the substrate. For this case, both HAADF and ABF approaches are valid to visualize the sites of individual atoms within a dumbbell, as shown in Figure 1A,C. In Figure 1A, the dumbbell...
positions show bright contrast, with the most intense spots corresponding to the heaviest element (Z-contrast images). On the other hand, ABF-STEM images (Figure 1C) offer an inversion of contrast with the atomic columns shown as dark spots, where the darkest correspond to the heaviest elements. These two methods are not only capable of visualizing the polarity of the NWs but also allow unambiguous differentiation of the different polytypes (dependence on the atomic plane stacking order, Figure S3)50 occurring along the NW growth direction. It should be noted that the presence of a twin in the ZB structure creates a single monolayer of WZ at the boundary. Thus, many consecutive twins may lead to the formation of WZ or some other polytypes if the periodicity is lower. In the past few years, a great debate has been generated on the search for new optoelectronic properties of the NWs when intermixing of polytypes could be synthesized to create superlattices.16,51–54 Unambiguous determination of the polytypes formed in the NW growth should conclude the debate on the existence of hexagonal silicon (type IV) in NWs.10,11,34,55,56 It is important to remark here that, due to the extremely small depth of field implied in aberration corrected HAADF-STEM images (which is not the case in HRTEM images), the atomically resolved area only includes a small thickness portion of the NW of a few nanometers. As a consequence, the image is not interfered by other planar defects occurring above or below the focal plane,57 thus unequivocally resolving the atomic structure. Taking into account that the brightest (darkest) contrast spots correspond to the heaviest atoms (Te) in HAADF-STEM (ABF-STEM), it is possible to directly visualize the polarity on the acquired images. In order to unambiguously differentiate the atomic positions within the dumbbell, intensity line profiles have been acquired along the dumbbell positions (Figure 1B,D). According to our present results, we can point out that the polarity on ZnTe NWs is always such that Te faces toward the nanowire tip (Te-polarized, see in Table 2 for the complete list of polarities observed for every studied material). Furthermore, despite the multiple twin defects leading to the different polytypic structures, the polarity is maintained across the twin boundaries, thus having only orthotwins instead of the inverted polarity paratwins.2,12,58 The distance between the Zn–Te dumbbell pairs measured by using both techniques (0.15 nm) is in good agreement with the atomic distance expected from theoretical calculation (Table 1).59

**MEDIUM AND SIMILAR ATOMIC NUMBER**

An example of a compound semiconductor formed by elements of medium and similar atomic number is GaAs. Here, we present the first polarity study on GaAs NWs exhibiting a modulated polytypic structure, grown by the gallium-assisted technique with molecular beam epitaxy. The growth conditions...
of the nanowire (e.g., growth rate) have been varied in order to modulate the crystal structure. In Figure 2A, a low resolution transmission electron micrograph of the nanowire is presented. Separated extended regions of WZ and ZB as well as the presence of some other multiple twinned regions with intermixed polytypes are indicated. The study has been performed on one of the highly twinned regions. In Figure 2B, the HAADF STEM image unveils perfectly separated Ga−As dumbbell pairs. A detail of the raw data is shown in Figure 2C. The intensity profiles have been obtained on each of the dumbbell pairs, as the one shown in Figure 2E. Here, the difference in intensity between the Ga and As is clearly observable, providing the path for the elemental mapping of the dumbbells.

In Figure 2D we show a temperature colored detail of the same region shown in Figure 2C, resulting in an elemental image. This measurement indicates that the polarity on GaAs NWs is such that As atoms are facing the tip (As-polarized, growth direction (111)B, see Table 2), as it was found in homoepitaxy experiments. Moreover, we find that similar to the case of ZnTe, the polarity across the twin boundaries is always kept, thus corresponding to orthotwins. The distance between the Ga−As dumbbell pairs corresponds to 0.14 nm, in good agreement with the calculated values (Table 1).

To further highlight the importance of twin defects in nanowires —thus the need of a reliable experimental technique to identify them, we have performed first-principles electron transport calculations to assess the impact that polar (paratwin) and nonpolar (orthotwin) twin defects have on the conductance of GaAs NWs. The electronic structure is calculated within density-functional theory as implemented in the Siesta code and the conductance is calculated following Landauer theory. We have found that in presence of nonpolar defects the conductance is almost entirely preserved at the band-edges. Polar twin defects, on the other hand, lead to a complete suppression of the conductance in the upper 0.3–0.4 eV of the valence band and a stronger reduction, compared to nonpolar defect, elsewhere (see the Supporting Information for full details of the calculations and a more extended discussion, see also Figures S4 and S5).

Table 2. Polarity as Observed for ZnTe, GaAs, ZnO, GaN, and AlN

<table>
<thead>
<tr>
<th>NW material</th>
<th>ZnTe</th>
<th>GaAs</th>
<th>ZnO</th>
<th>GaN</th>
<th>AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td>polarity (the element which is facing the tip)</td>
<td>Te</td>
<td>As</td>
<td>Zn</td>
<td>N</td>
<td>N</td>
</tr>
</tbody>
</table>

**a** The polarity is given by the element that faces the tip of the NW, this element shows the termination of the {111} or {0001} growth planes, when the NW is in ZB or WZ phase, respectively.

Figure 3. (A) HAADF-STEM general view of one of the studied ZnO NWs. (B) Atomic resolution aberration corrected HAADF-STEM detail of the ZnO WZ structure in a selected region of the NW in A. (C) Atomic resolution aberration corrected ABF-STEM detail obtained on the same area as in B. (D) ABF-STEM magnified detail of the region marked with an orange rectangle in C. (E) Temperature colored detail of the same region in D. (F) ABF intensity profile obtained across the Zn−O dumbbell pair inside the red rectangle region in C. The red arrow in C and F points to the profile direction.
In the characterization study shown in Figure 3, we compare again the images obtained from HAADF-STEM (Figure 3B) with that obtained from ABF-STEM (Figure 3C). Contrary to the ZnTe example shown in Figure 1, in the present case, HAADF-STEM cannot resolve the dumbbell pairs in the structure due to the low Z number of the oxygen atoms (Figure 3B). However, in Figure 3C, the ABF-STEM image perfectly shows the presence of a lighter contrast zigzag below the darker atomic positions (Zn). Zoomed-in view of the nanowires with ABF-STEM is shown in Figure 3D and 3E, with raw ABF-STEM signal and applied temperature coloring, respectively. The Zn atomic positions perfectly coincide in both, HAADF-STEM and ABF-STEM techniques.

In addition, the lightest contrast observed on the ABF-STEM images is placed at 0.12 nm from the Zn position (Figure 3C–F), which is in perfect agreement with the expected Zn–O dumbbell pair separation distance (Table 1). Intensity profiles obtained along the dumbbell pairs clearly confirm the 0.12 nm dumbbell pair distances (Figure 3F). Direct observation of the dumbbell pairs reveals all the required information about the NW polarity. The growth of the ZnO NWs analyzed here occurred along the +[0001] axis with O on the base and Zn pointing to the tip. This Zn polarized growth (Table 2) is in good agreement with previous works based on indirect measurements.19

Finally, in order to explore the spatial and chemical resolution limits of the ABF STEM, we have considered the study of the polarity in GaN NWs grown on Si(111) as well as of polarity transfer in a GaN-AlN core–shell NW heterostructure. This study, visualized in Figure 4, has been performed on a GaN/AlN NW heterostructure (Figure 4A), grown by plasma assisted molecular beam epitaxy (PAMBE) on Si (111) using nitrogen-rich growth conditions as reported elsewhere.66

In Figure 4B the sharp interface between the GaN core and the AlN shell is displayed. Despite the low interatomic distance within the Ga–N and Al–N dumbbell pairs (barely 0.11 nm in both cases, Table 1) and the low Z value of the N atoms (Table S1), the polarity can be resolved with atomic resolution. The first important result to point out is that the GaN core has a wurzite (WZ) structure with the nitrogen atoms pointing to the tip (N polarized (N-face polarity), Table 2), and that this polarity is transferred to the shell material (AlN). Due to this perfect transfer the AlN part maintains the same polarity with the (0001) planes terminated by N atoms (N-face polarity). A perfect epitaxial relationship occurs between both materials resulting in a perfectly abrupt interface as shown in Figure 4B–E. The measured distances between the dumbbell pairs in both, Ga–N and Al–N, are exactly 0.11 nm, in good agreement with the expected 0.109 nm, as calculated in Table 1. It should be noticed that the polarity of the GaN NWs can depend on the growth process, the substrate material and the nucleation conditions as well as the presence of buffer layers. This might explain the apparent contradiction to the results presented in other works. In ref 67 the N-face polarity of GaN NWs grown by PAMBE on Si (111) was determined by channeling-enhanced electron energy loss spectroscopy and CBED, whereas growth on an AlN buffer was found to result in Ga-face polarity. In contrast, N-face polarity was found for PAMBE-grown GaN NWs on both bare Si (111) substrates and AlN buffer layers using resonant X-ray diffraction.68 Ga-face polarity was found for GaN NWs grown by ammonia-molecular beam epitaxy on Si(111) using CBED69 and also for GaN NWs grown on Si(111) by PAMBE employing also

![Figure 4. (A) HAADF-STEM general view of the studied GaN-AlN NW heterostructure. (B) Atomic resolution aberration corrected ABF-STEM detail of the GaN-AlN WZ heterostructure in a selected region of the NW in A. (C) ABF-STEM magnified detail of the squared region in B. (D) Temperature colored detail of the same region in C. (E) ABF intensity profile obtained across the Ga–N and Al–N dumbbell pairs inside the red rectangle region shown in B. Notice that we have obtained one profile for the N column (red profile) and a second one for the Ga and Al atomic columns (blue profile), see corresponding red and blue dashed line profile position in B.](image)

**LOW ATOMIC NUMBER**

We have demonstrated with two examples that the HAADF-STEM is an excellent tool for resolving the dumbbell pairs. A more challenging task is the resolution of light elements such as O and N, which are in fact two of the elements of major interest for a wide sector of the semiconductor community, as it includes technologically relevant materials such as ZnO or GaN/AlN. In the case of ZnO, one of the most frequently used materials in NWs semiconductors research,62–64 there is a longstanding debate on how to measure its polarity. The polarity study illustrated in Figure 3, has been performed on a ZnO NW (Figure 3A), obtained by a vapor transport technique,67 with the layered-structured muscovite mica as the substrate to achieve a well-crystallized heteroepitaxial growth via the van der Waals epitaxy mechanism,68 similar to those reported elsewhere.65

![Diagram](image)
analysis by CBED.\textsuperscript{70} Here we show the importance of a direct visualization technique that can unambiguously determine the dumbbell composition and thus the NW polarity.

As a conclusion, we have presented two powerful tools, namely HAADF and ABF STEM imaging, which can be applied for the direct determination of the dumbbell polarity in compound semiconductor nanowires. Both techniques could be applied to any other nanostructure, such as nanoparticles, interfaces, thin film heterostructures and extended to any other material, such as complex oxides, where the possibility of imaging oxygen is priceless. Up to our knowledge, it is the first time that polarity can be imaged directly on semiconductor NWs where one of the constituent elements of the dumbbell is a light element (e.g., O or N), which is the case for ZnO, GaN, and AlN. One of the most interesting results is that after analyzing several twin boundaries in different semiconductor nanowires (mostly of ZnTe and GaAs) we could never find a change in polarity across twin boundaries. Fortunately, the presence of nonpolar twin boundaries (orthotwins) do not significantly modify the electronic structure of the material and its conductivity, in sharp contrast to the presence of polar twins (paratwins) which would drastically reduce the conductance, as demonstrated theoretically in the present work.

Future studies should include the characterization of more complex heterostructures such as the heterointerface between polar and nonpolar materials.

**ASSOCIATED CONTENT**

Supporting Information
ABF and HAADF STEM experimental set up and conditions, description of the polytypic species in semiconductor materials and first-principles calculations: electronic structure and conductivity. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was partially supported by the Spanish Project Consolider Ingenio CSD2009 00013 IMAGINE and CSD2009 00050 MULTICAT. J.A. acknowledges the funding from the Spanish MICINN Projects MAT2010-15138 and MAT2010-21510 and Generalitat de Catalunya (2009 SGR 770, NanoAraCat and XaRMAE). M.H. and A.F.i.M. thank funding through the ERC starting Grant NanoAraCat and XaRMAE). M.H. and A.F.i.M. thank funding from Project DOTSENSE (FP7, Grant No. 224212).

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(26) The atomic distances between the dumbbell elements have been calculated by using the Carine 3.1 Crystallography software.


