Crystallographic Mapping of Guided Nanowires by Second Harmonic Generation Polarimetry

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Supporting Information

ABSTRACT: The growth of horizontal nanowires (NWs) guided by epitaxial and graphoepitaxial relations with the substrate is becoming increasingly attractive owing to the possibility of controlling their position, direction, and crystallographic orientation. In guided NWs, as opposed to the extensively characterized vertically grown NWs, there is an increasing need for understanding the relation between structure and properties, specifically the role of the epitaxial relation with the substrate. Furthermore, the uniformity of crystallographic orientation along guided NWs and over the substrate has yet to be checked. Here we perform highly sensitive second harmonic generation (SHG) polarimetry of polar and nonpolar guided ZnO NWs grown on R-plane and M-plane sapphire. We optically map large areas on the substrate in a nondestructive way and find that the crystallographic orientations of the guided NWs are highly selective and specific for each growth direction with respect to the substrate lattice. In addition, we perform SHG polarimetry along individual NWs and find that the crystallographic orientation is preserved along the NW in both polar and nonpolar NWs. While polar NWs show highly uniform SHG along their axis, nonpolar NWs show a significant change in the local nonlinear susceptibility along a few micrometers, reflected in a reduction of 40% in the ratio of the SHG along different crystal axes. We suggest that these differences may be related to strain accumulation along the nonpolar wires. We find SHG polarimetry to be a powerful tool to study both selectivity and uniformity of crystallographic orientations of guided NWs with different epitaxial relations.

KEYWORDS: Guided nanowires, zinc oxide, second harmonic generation, polarimetry, strain

The guided growth of horizontal nanowires (NWs), in which assembly and alignment of the NWs are achieved during the growth process, is attracting growing interest due to the unique opportunity to eliminate the need for post-growth processes as well as to gain deterministic control over their position, direction, and length. Since its first demonstration by Nikoobakht and co-workers, an increasing number of reports can be found on the growth of horizontal NWs and their direct integration into planar devices. A vapor–liquid–solid (VLS) process, guided by the surface, yields horizontal NWs with controlled directions and crystallographic orientations, determined by the epitaxial and graphoepitaxial relations with the substrate. Based on what is known from bulk and thin films, the crystallographic orientation and epitaxial relations with the substrate are expected to play an important role in determining the electronic and optical properties of NWs. Therefore, the guided growth of horizontal NWs can be used as a way of controlling NWs properties. However, in order to fulfill the potential of the guided growth approach as a method to produce large arrays of aligned NWs with known properties, the selectivity and uniformity of crystallographic orientations of guided NWs must be studied.

The mechanism that drives the growth of lateral NWs is not yet well understood. A few models describing vertical vs horizontal growth have been proposed, but as continuum models, they do not consider the effect of epitaxy. The results accumulated so far indicate that the growth of horizontal NWs is strongly affected by epitaxial relations with the underlying substrate, but what exactly determines the growth direction and crystallographic orientation is not yet known nor can it be predicted. For example, in vapor–solid (VS) planar growth of quasi-1D islands, there is a preferred elongation along the direction with the lowest mismatch. On the other hand, in VLS growth in systems with high lattice mismatch and low lattice symmetry, the lowest mismatch is found across the NW rather than along it. In systems where the overgrown crystal and the substrate belong to the same crystal family and have a relatively low lattice mismatch, planar NWs are relatively well matched in both longitudinal and transversal directions. In this case, it is difficult to determine the direction in which lattice matching is more important, and NWs can grow in different
directions on the same substrate. Moreover, in cases where more than one crystallographic orientation is stable enough to form in a certain direction, the uniformity of the crystal orientation along the growth direction of the same NW cannot be taken for granted, and the question whether guided NWs sustain their crystallographic orientation along the growth axis remains an open one.

As opposed to vertical NWs, which can be placed on a grid and examined by high-resolution transmission electron microscopy (HRTEM) to determine the crystallographic orientation, guided NWs lay strongly bound to the substrate. Therefore, their structural characterization by TEM is more challenging, usually requiring the preparation of a thin electron-transparent lamella across the NWs using a focused ion beam (FIB). This method has a few major drawbacks: (i) it is completely destructive, (ii) it is extremely time-consuming, (iii) it is limited to a small region on the substrate, (iv) when cut across the transverse direction of the NWs, only one very specific position along the NWs is probed, and (v) when cut along the NW growth direction, only a single NW is probed. Optical noninvasive methods for structural study, such as Raman spectroscopy, can be highly effective for the determination of crystallographic orientations when performed on free-standing NWs placed on a substrate of choice but are very challenging in the characterization of guided NWs due to the strong signal from the substrate. It is thus important to develop a fast, robust, noninvasive, and highly sensitive structural characterization method to study guided NWs over large areas and along single NWs.

SHG has become widely used for the study of crystalline structures, specifically nanostructures, where direct structural probing becomes more challenging and where phase matching considerations are absent. Since SHG strongly depends on polarization, polarimetric measurements can serve as the tool of choice for highly sensitive structural studies. The fast measurement, which allows statistical study on a large number of nanostructures at the single nanostructure level, its non-destructive nature, and the rather simple optical setup have rendered this tool very useful for crystallographic characterization. Several studies in recent years have used SHG to determine crystal phase, crystal orientation, and defects within nanostructures of many types, such as quantum dots, NWs, and molecular crystals. Nevertheless, to the best of our knowledge, SHG polarimetry has not yet been used to study horizontally grown NWs. This method should be particularly interesting where more than one growth direction exists, to study the effects of different epitaxial relations with the substrate on the growth direction and crystallographic orientation.

We showed before that ZnO NWs can grow horizontally in a wurtzite (WZ) structure on various smooth and faceted sapphire substrates. Specifically, guided ZnO NWs on M-plane (1010) sapphire grow in four perpendicular directions, ⊥[1210]Al₂O₃ and ±[0001]Al₂O₃, yielding two types of NWs, termed either polar or nonpolar. “Polar” wires are those which grow in the direction of the crystalline polarity (c-axis, i.e., [0001]ZnO). “Nonpolar” wires are those who grow perpendicular to the direction of crystalline polarity (e.g., [1210]ZnO). Note that these wires exhibit the same polar structure and are only nonpolar along the growth axis. As a result of these respective relations, the longitudinal lattice mismatch of the polar NWs (9.34%) is the transverse lattice mismatch of the nonpolar ones, and vice versa (0.02%). For guided ZnO NWs, the two mentioned options are stable enough to form under the same growth conditions. This unique system provides us with the opportunity to study the effect of NW–substrate mismatch along the growth axis of epitaxial guided NWs on their structure and orientation.

In this work we use SHG polarimetry to investigate guided ZnO NWs grown on different sapphire planes. As a first step, we confirm the structure of the ZnO crystal and determine its Euler angles with respect to the lab frame. We map a large area of our samples and find a high selectivity and specificity in the crystallographic orientations of the NWs with respect to the substrate lattice directions along which they grow ([0001]ZnO along ±[1210]Al₂O₃ and [1210]ZnO along ±[0001]Al₂O₃). We determine that the crystallographic orientation along the growth direction of both polar and nonpolar NWs is kept constant throughout their entire length. To quantitatively analyze the SHG along guided NWs, we include the geometry of the NW cross section and the dielectric field distribution inside the NW. Polar NWs show a highly uniform SHG polar distribution along their growth axis, whereas nonpolar NWs show gradual but significant change. Uniform and nonuniform photoluminescence (PL) spectra along the same polar and nonpolar NWs, respectively, are consistent with these results. We attribute these differences to strain, either accumulated or relaxed according to the different lattice mismatch in the two growth directions. Small lattice variations are detectable owing to the very high sensitivity of SHG polarimetry to any changes in the structure and symmetry of the hexagonal crystal.

Guided ZnO NWs were grown by chemical vapor deposition from Au catalyst, on R (1102) and M (1010) planes of sapphire by a previously reported process, slightly modified (see Supporting Information for synthesis details). After the synthesis, the guided NWs were characterized by scanning electron microscopy (SEM). NWs grow horizontally and aligned from the gold nanoparticles. Their diameters were found to be in the range 30–80 nm, and their typical length is around 10 µm. Figure 1a shows a typical SEM micrograph of guided ZnO NWs on R-plane (1102) sapphire. NWs grow with polar [0001]ZnO orientations along two opposite directions ±[1101]Al₂O₃. On M-plane (1010) sapphire (Figure 1b) the guided NWs with polar [0001]ZnO orientation grow along the nonpolar ±[1210]Al₂O₃ direction and NWs with a nonpolar [1210]ZnO orientation grow along the polar ±[0001]Al₂O₃ direction.

We use SHG polarimetry for the crystallographic study of guided NWs. The second harmonic induced (SH) polarization is described by P(2ω) = ε0d(2)E(ω)E(ω). Here, E(ω) and E(ω) stand for the two fundamental fields with frequency ω, and d(2) is a rank 2 tensor for the second-order nonlinear susceptibility. It is more convenient to work with the contracted rank 2 representation P(2ω) = 2ε0d(2)E(ω)², where E(ω)² = (Eₓ², E_y², E_z², 2EₓE_y, 2EₓE_z, 2E_yE_z) and d is a 3 × 6 matrix for the second-order nonlinear susceptibility. Every crystal structure is characterized by a different d matrix, which determines the SH response to the inducing fields. For the WZ structure (6mm symmetry group) the d matrix contains only three independent elements and has the general form of

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 \end{pmatrix}$$
When Kleinman symmetry applies (corresponding, in this case, to the absence of a two-photon absorption resonance), then $d_{15} = d_{31}$, and the $d$ matrix contains only two independent elements $d_{15}$ and $d_{33}$.\footnote{The contribution of these elements manifests itself in the SHG response. To individually measure these matrix elements, one needs to change the polarization of the inducing laser and measure the intensity of the induced SH polarization. The obtained curve is then fitted to a model considering the magnitude of the tensor elements, the crystal shape, and its spatial and crystalline orientation. Since the crystallographic orientation relative to the lab frame directly affects the measured SHG, in many cases this orientation can be identified. SHG is well described by the above equations, so it is possible to simulate the measured SH intensity as a function of polarization angle (after a detailed consideration of all the needed corrections). Fitting the best simulation to the measured data is used to determine the structure and crystalline orientation. More details about simulation and fitting can be found in the Supporting Information. SHG in noncentrosymmetric nanostructures can originate from both its surface and volume. Nevertheless, surface SHG is far less efficient and is more pronounced in centrosymmetric nano-objects.\footnote{In the case of semiconductor quantum dots, it has been shown that the bulk contribution dominates over the surface for diameters as small as 5 nm.\footnote{Thus, for the sizes of NWs discussed here, the volumetric SHG contribution greatly exceeds the surface contribution, and we can safely ignore the latter. We also note that the sapphire substrate (symmetry group 3m) has a vanishing $\chi^{(2)}$ and hence does not significantly contribute to the measured SHG signal.\footnote{Nevertheless, we show below that the presence of the sapphire substrate does affect the field distribution inside the NW and thus plays a significant role in the SHG from guided NWs.}}}

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 \\ d_{15} & d_{15} & d_{33} & 0 & 0 \end{pmatrix}$$

Figure 1. Guided ZnO nanowires with controlled orientation on different sapphire substrates. SEM micrographs of ZnO NWs grown on (a) R-plane sapphire and (b) M-plane sapphire and their corresponding crystalline orientations described by the inset. Scale bars are 2 μm.

For Figure 2a we describe our experimental setup used for SHG polarization measurements. We employed an 80 MHz, 100 fs, Ti:sapphire pulsed laser at wavelength of 950 nm to generate SH from a single ZnO NW. The excitation wavelength was chosen so as to avoid two-photon absorption and thus fulfill the Kleinman symmetry conditions. The sample was placed facing down on top of a glass coverslip, to eliminate the effect of birefringence of the sapphire substrate, in an inverted microscope with an x-y piezo stage. The laser beam was passed through a rotatable half-wave plate and focused on the sample using a 20×, 0.5 NA objective lens. We chose low NA to avoid excitation and detection of out-of-plane dipoles, yet not too low to deteriorate the optical resolution and the signal collection efficiency. The fwhm of the beam diameter at the focal point was measured to be 1.2 μm. The induced SHG light at 475 nm was epi-detected, filtered, and sampled through a linear polarizer (analyzer). A fiber-coupled single-photon detector (SPD) connected to a time-correlated single-photon counter (TCSPC) was used to measure and count the photon flux. The input polarization was rotated while the analyzer sampled the two perpendicular polarizations, x and y.

Typical polar plots, in which SH intensity is plotted as a function of polarization angle, can be seen in Figure 2c–e, where the blue line represents x-polarized SHG signal and the red line is the y-polarized signal. It should be noted that the symmetry of the polar plots (e.g., two-lobed or four-lobed) does not directly reflect the symmetry of the crystal, but rather on a specific projection onto the lab x-y plane. The observed patterns are indeed characteristic of the WZ crystal structure. The lab frame of reference was such that the sample plane was specified as x-y and the laser propagation as z. To interpret the polarimetric results and find the crystal orientation, we have used rotation matrices in the $z'−y'−z''$ convention to rotate the frames of reference between three frames: lab, NW, and crystal (for more details see the Supporting Information). The inducing and induced fields were projected on these axes frames. The NW frame is defined by the long axis of the NW. The crystal frame is defined by the three angles $\alpha$, $\beta$, and $\gamma$, describing the main crystallographic axes of the crystal relative to the lab frame (the angles are illustrated in Figure 2b). After determining the orientation of the c-axis of the WZ structure, the sample was rotated such that it aligns with the x-direction of the lab frame. This way, the polar wires (either on R- or M-plane) were aligned along the lab x-axis, and the nonpolar NWs on M-plane were aligned along the lab y-axis. (see Figure 2a). The dramatic differences between polar and nonpolar wires seen in Figure 2d,e are mostly due to a geometric effect as discussed in detail below.

To study the selectivity of crystallographic orientations throughout the sample, we use the $x−y$ nanometric stage and scan large areas of the sample at a fixed polarization. Figure 3a shows such a large area ($30 \mu m \times 50 \mu m$) scan of guided ZnO NWs on R-plane sapphire. The polarization angle for excitation and detection was chosen to be $0^\circ$ (along the x-axis) to maximize the intensity. Very long ZnO NWs sometimes exhibit a gently tapered shape due to the addition of material from the gas phase directly to the solid side-walls of the wire. This can be related to a gradual drop in the SHG intensity (due to the reduction in excitation volume) along the longer NWs in Figure 3a. Figures 3b...
and 3c present medium and small area scans on M-plane, where both polar and nonpolar NWs are observed. In this sample, the wires are relatively shorter and care was taken to measure NWs with no significant height variation along them as measured by AFM. Figures 3b and 3c show that the SHG intensity is highly uniform along the wire. After mapping a desired area, we use the piezo stage to position the laser beam at a certain point and acquire a polarimetric measurement to determine the crystal structure and orientation. More than 50 different NWs were examined by SHG polarimetry on both R- and M-planes. All showed a four-lobed shape, typical for the 6mm point group. The detection of the small lobes in polar NWs is difficult to achieve due to the strong reduction of the signal perpendicular to the c-axis (Figure 2d). The high stability of the ZnO NWs in air and the choice of excitation wavelength far from resonance enable the use of high laser intensities. Along with the use of TCSPC, the result is a very high signal-to-noise ratio, which allows us to explore the ratio of the lobes for the polar NWs and compare to the nonpolar NWs. Fitting the four-lobed shape of the SHG polarimetry to a simulation confirmed that indeed all NWs have a WZ structure with their c-axis pointing along the ±[110]Al2O3 or the ±[210]Al2O3 directions of the R- and M-plane sapphire, respectively. The orientations found are consistent with our HRTEM results on a thin slice along both polar and nonpolar NWs (Supporting Information) and the thorough crystallographic analysis previously reported. These findings show very high selectivity of crystallographic orientations on two different planes of sapphire and indicate a highly selective growth process driven by epitaxial relations with the substrate.
Although the crystal polar axis points to the same direction with respect to the lab frame, in the polar NWs it aligns with the long axis and in the nonpolar ones with the in-plane short axis. This results in a fundamental difference between the nonlinear response of polar and nonpolar NWs. Under the electrostatic approximation, the effective electric field inside a dielectric cylinder becomes \( E = E_0 + fE_1 \). Here, \( E_0 \) and \( E_1 \) are the fields parallel and perpendicular to the long cylinder axis just outside the cylinder, and \( f = 2/(1 + \epsilon_m/\epsilon_0) \) is the reduction factor in the perpendicular direction. \( \epsilon_m \) and \( \epsilon_0 \) are the medium and the environment dielectric constants, respectively. Similarly to the perpendicular field reduction at excitation, this 1D geometric effect also reduces the strength of the induced SHG fields in the same direction, with the appropriate dielectric constant for the doubled optical frequency \( \epsilon(2\omega) \). Since the field is reduced twice in this second-order process, the consideration of the geometric effect becomes highly significant when analyzing SHG from NWs. For example, when excitation and detection are both done parallel to the long axis, SHG is not affected. However, when both excitation and detection are along the short axis, the most drastic reduction occurs \( (|2\omega|/\omega_0)^2 \). Here, we experimentally show an example of the strength of this 1D geometric effect. Our measurements show that the ratios between the SHG intensity excited by \( x \) and \( y \) polarizations \( (|0\omega|/(90\omega)) \) are extremely different for the bulk sample, polar NWs, and nonpolar NWs: typically 8, 100, and 1, respectively (Figure 2c–e).

The electrostatic approximation applied above is valid when the wavelength of light \( \lambda = \lambda/2\pi \) inside the medium is much larger than the diameter \( a \) of the NW. Unlike recent work on tapered nanobelt, \(^5\) where the geometrical field factor along a nanobelt as a function of its width was inferred, here we work in the regime of \( a \ll \lambda_{uv} \) where \( f \) does not depend on diameter. All the NWs examined in this paper have diameters well below the wavelength inside the medium. Their height was measured using AFM and found to be less than 80 nm. Overall, TEM cross-sectional analysis in previous study\(^7\) indicates that the width is not larger than 50 nm. As a consequence, we have limited ourselves to a size-independent factor for all NWs.

Another effect that needs to be addressed is that guided NWs are in contact with a dielectric substrate \( (\epsilon_0 = \sim 3.1 \) for sapphire at optical frequencies\(^8\)). Therefore, they cannot be treated as a cylinder in vacuum. In order to obtain the appropriate factor \( f \), we performed a simulation of the electrostatic fields inside a trapezoidal cross section (Figure 4b), typical of ZnO NWs lying on a sapphire substrate with growth orientation [0001] \( ZnO \) as can be seen from the cross-section TEM image (Figure 4a). Although only a minute distortion of the directions of the fields near the edges and corners was observed, the field strength was not uniform as in the case of cylindrical cross section in vacuum. The averaged field reduction factors for a guided ZnO NW were found to be 0.62\(_{w} \) and 0.59\(_{b} \), significantly higher than 0.42\(_{w} \) and 0.38\(_{b} \) obtained for a cylinder in a vacuum. This substrate dielectric effect is significant when interpreting the SHG polarimetric response of nanostructures; nevertheless, it is often disregarded or being misused in analyses. Figure 4c shows the importance of taking the correct field factor by plotting fits to data of the two cases discussed above: trapezoidal cross section of ZnO NW on a sapphire substrate and ZnO cylinder in vacuum. Given a reasonable constant value of \( d_{15}/d_{33} = -0.33 \), it is clear that selecting the right factor is important for getting better quantitative understanding. The polarimetry measurement, however, cannot be solely explained by the geometrical correction without considering an effective modification of the \( d \) matrix elements ratio \( (d_{15}/d_{33}) \) as well.

Each polarimetric measurement was fitted with simulation of three angles of crystalline orientation \( \alpha, \beta, \) and \( \gamma \) (although \( \gamma \) has no effect on the SHG from \( 6\)mm symmetry group), the effective \( d_{15}/d_{33} \), noise, and a global amplitude as free variables. Our simulation accounts for the local field reduction at both the fundamental and SHG fields as well as for the collection efficiency of the SHG dipole radiation by our objective at both detection polarizations and for input power differences between polarizations (more details can be found in the Supporting

![Figure 4. Effect of substrate and cross section on the SHG of guided NWs. (a) TEM micrograph of guided ZnO NW on M-plane sapphire. Scale bar is 10 nm. (b) Simulated field for a cross section of a ZnO NW, lying on a sapphire substrate in air. The white arrows and the color scale represent the field vectors and normalized intensities, respectively. Intensity value of unity stands for the unperturbed field. (c) The \( x \)-polarized signal of a polarimetric measurement of a nonpolar NW (blue line) and geometrical factors of cylinder in vacuum (purple dashed line). The fit was done using a constant ratio of \( d_{15}/d_{33} = -0.33 \).](image-url)
As mentioned earlier, we work in the range of \( a \ll \lambda_w \) where \( f \) does not depend on diameter and SHG in these sizes is mainly a function of the volumetric \( \chi^2 \). In addition, AFM scans along the NWs did not reveal any gradual change in thickness. Thus, the change along nonpolar NWs cannot be explained by geometric change along these wires. In principle, the gradual change of the intensity ratio between the vertical and horizontal lobes can be explained by a rigid rotation (constant \( d_4 \)) of the crystal. Using our simulation and assuming a rigid rotation along the NW, we found that only rotation of the \( c \)-axis around the long axis of the NW, by allowing \( \beta \) to change along the NW, could explain the observed change presented in Figure S5b. In order to quantitatively account for the observed change, the \( c \)-axis should be allowed to rotate 15–20° along 5 \( \mu \)m. To examine this possibility, we cut a longitudinal lamella along the same NW and examined it using HRTEM. We found no evidence for such rotation of the \( c \)-axis. In fact, no evidence for any rotation was found by examining FFT of the HRTEM micrographs taken at several points along the NW. Thus, we conclude that the crystallographic orientation is preserved along the NW and that the gradual change has a different origin, presumably involving a change in the \( d \) matrix elements along the NW.

The fact that the two types of wires grow under the exact same conditions suggests that growth in different directions along the substrate affect the SHG not only in dictating the crystallographic orientation but also by introducing strain according to the different lattice mismatch in the two directions. SHG is extremely sensitive to crystallographic deformation, as shown in a recent report that underscored the high sensitivity of SHG polarimetry to smallest strains in the order of 10^{-9} nm.16 Both contraction and stretching are expected to compromise the symmetry of the...
Crystal and thus change the values of the $d$ matrix elements. Contraction or stretching of the unit cell in the longitudinal direction also cause stretching or contraction in the transverse direction, respectively, according to Poisson ratio. Accordingly, the main axes of the crystal perpendicular to the $c$-axis ($x$ and $y$ of the crystal) are not symmetric as in unstrained ZnO, and hence the $6mm$ point group symmetry is reduced to $2mm$. Under the $2mm$ symmetry, there are three independent matrix elements: $d_{15}$, $d_{23}$, $d_{33}$. Unfortunately, when examining the equations the fact the $c$-axis lies in the sample plane is hindering us from inferring both of the ratios $d_{15}/d_{33}$ and $d_{23}/d_{33}$, but rather these are reflected in a single measurable parameter $d_{eff} = (d_{15} \cos^2 \gamma + d_{23} \sin^2 \gamma)/d_{33}$. Recalling $\gamma$ is the angle of rotation around the $c$-axis. Strain was also shown to remarkably deform both the ZnO NWs and the substrate when grown on $A$-plane sapphire. $12$ Similarly, NWs in this work are expected to maintain some level of strain. This could explain the variation of the $d$ matrix elements ratio along the nonpolar NWs despite the preservation of the crystallographic orientation along them.

Interestingly, the variation of $d_{15}/d_{33}$ along the wire, which is prominent in nonporal wires, is absent from the polar wires. This may be attributed to the fact that the $M$-plane sapphire substrate mismatch with the crystalline ZnO is found to be very different in the two directions observed, dictating different epitaxial relations that can affect strain accumulation or relaxation. For example, in ZnO thin films on $R$-plane sapphire, the strain fully relaxes in one direction through misfit dislocations, while in the perpendicular direction strain remains. $62$ In guided NWs that grow in two perpendicular directions with the reverse longitudinal and transverse mismatch values, we can expect different strain accumulation along the two types of wires. If the longitudinal strain is initially too low to be relaxed by misfit dislocations, it can accumulate as the wire grows longer and deform the crystal further and might lead to the observed gradual change for the nonpolar wires. To examine this possibility, we cut a longitudinal lamella along both polar and nonpolar NWs and performed HRTEM study. We found that indeed in the polar NW periodic misfit dislocations appear in a $11:12$ ratio, which is in good agreement with the mismatch in this direction, indicating a strain relaxation mechanism. For the nonpolar NWs, the interface could not be inspected in details due to a blurry region in the lamella. We have tried to find any structural changes along them, specifically by measuring the interplanar distances at several points along the wires; however, the TEM analysis shows no change in the lattice parameters along the wire within the error range (more details and results can be found in the Supporting Information). This may indicate that SHG polarimetry is sensitive to very small strains, beyond the accuracy of our HRTEM measurements.

Despite the lack of information provided by TEM regarding the gradual change of SHG along the nonpolar NWs, PL measurement turn out to be more revealing. PL in ZnO may originate from both the near band-edge emission (NBE) at wavelength of $\sim 380$ nm and also from various defect states emissions (DSE). Such states include interstitial atoms and vacancies of both Zn and O in many electronic charge configurations. $63$ The DSE is wide in spectrum and appears around $450\text{–}700$ nm. PL of defects in NWs is attributed mostly to surface states due to the rather high surface-to-volume ratio for defects concentration and enables the exploration of the properties of the surface. PL measurements were done using a micro-Raman/micro-PL system (Horiba LabRAM HR Evolution). A $325$ nm laser was focused on the NW through a reflective objective lens. PL was collected using the same objective and sent to a $300$ lines/mm grating and an EMCCD camera. Image processing produced a calibrated spectrum. The wires were scanned with a piezo stage and at each position a spectrum was acquired. Both polar and nonporal wires were oriented in the same direction to avoid different excitation due to the objective lens shape. The NBE of both polar and nonporal NWs is observed at $\sim 375$ nm, slightly blue-shifted from the typical $380$ nm emission of ZnO. Quantum confinement can be ruled out because the diameter of the wires is larger than the exciton Bohr radius. We observed in the past that vertically grown ZnO NWs from the same sample, which are assumed to be strain-free, also show a slight blue-shift in their NBE. This indicates that the observed blue-shift is not due to strain. Alternatively, the blue-shift may be due to a Burstein–Moss effect, which was observed for small diameter ZnO NWs. $64$ This effect is relevant for both polar and nonporal NWs.

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**Figure 6.** PL along ZnO NWs. Photoluminescence spectrum of (a) polar and (d) nonpolar NWs. Longitudinal spectral scan of (b) polar and (e) nonpolar NWs. Visible spectra of two points along the wire for (c) polar and (f) nonpolar NWs.
The differences between the two types of NWs manifest themselves in the DSE emission. Results show that the ratio between DSE and NBE in polar NWs in both M- and R-planes (not shown) is much higher (Figure 6a,d), indicating that more electrons are trapped in defect states. In addition, PL area scans (Figure 6b,e) along the NWs exhibited more differences between polar and nonpolar wires. Here, we present the normalized visible spectrum along two wires, polar and nonpolar. In the former, the spectra seem very uniform, while in the latter, the spectra changes along the wire. A sharp variation in emission spectra is seen here and also in several other nonpolar wires examined. The uniformity and nonuniformity of PL from polar and nonpolar NWs, respectively, is consistent with the SHG polarimetric longitudinal scans. To further elucidate this observation, spectra in specific positions along the wire are displayed in Figure 6c,f. We consider those spectra variations to be dominated either by surface variations, such as different facets exposed at the surface, or induced by a change in oxygen vacancies and interstitials concentrations, with emission wavelength close to the 520 and 580 nm lines of oxygen defects. Although it may simply be a surface effect, this observation is yet another evidence of the nonuniform growth of the nonpolar NWs, in comparison to the polar ones.

To conclude, SHG polarimetry is found to be a powerful, noninvasive, and highly sensitive method for the characterization of guided NWs. Mapping of crystallographic selectivity over large areas of NWs assembly and along individual NWs, enables the study of crystallographic selectivity, specificity, and uniformity over the sample and along single NWs. We find that the guided growth of ZnO NWs on both R- and M-plane sapphire is highly selective and that crystallographic orientation is determined by the epitaxial relations with the sapphire. The crystallographic orientation was found to be preserved along the NW. The high sensitivity of SHG polarimetry to the crystal structure and symmetry uncovers previously unexplored differences between NWs epitaxial guided in different orientations, grown under the exact same conditions. While polar NWs are highly uniform, nonpolar NWs show gradual variation in their nonlinear properties along the growth direction. Variations in the photoluminescence along the NWs are consistent with the observation of the nonuniform SHG along the nonpolar NWs. Considering all of our findings and the nature of bulk SHG, we suggest that the changes in the nonpolar NWs polarimetric measurements along the wires may be related to crystal strain that is not fully relaxed in this growth environment and configuration. These findings indicate the important role of the substrate beyond the control over direction and orientation and show the relation between crystallographic orientation and properties of guided NWs. On the one hand, the fact that SHG polarimetry can be more sensitive to structural, compositional, mechanical, or electronic changes than other techniques (e.g., TEM, XPS, EDS, etc.) makes it difficult to independently identify the origin of certain SHG changes over different regions of the same sample. On the other hand, the ability to inspect a large number of NWs and detect small variations in crystalline nanostructures with an all-optical setup demonstrates the power of SHG polarimetry for similar studies.

ASSOCIATED CONTENT

Supporting Information

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Notes

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ABBREVIATIONS

NW, nanowire; VLS, vapor—liquid—solid; VS, vapor—solid; FIB, focused ion beam; HRTEM, high-resolution transmission electron microscope; SHG, second harmonic generation; NP, nanoparticle; SEM, scanning electron microscope; NA, numerical aperture; fwhm, full width at half-maximum; SPD, single-photon detector; TCSPC, time-correlated single-photon counter; AFM, atomic force microscope; PL, photoluminescence; NBE, near band-edge emission; DSE, defect state emission; EMCCD, electron multiplying charge-coupled device; TEM, transmission electron microscope; XPS, X-ray photoelectron spectroscopy; EDS, energy-dispersive X-ray spectroscopy.

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