Polarized and non-polarized Raman spectroscopy of ZnO crystals: Method for determination of crystal growth and crystal plane orientation for nanomaterials

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Abstract
Analysis and determination of crystal orientation and exposed surface facets remain a challenge in nanomaterial science. In this work, we show that polarized and non-polarized Raman spectroscopy can be useful tools to determine crystal plane orientation and conveniently be applied to spatial dimensions limited only by the diffraction limit of the excitation laser. The methodology is exemplified for wurtzite structured ZnO. Three different crystal facets, (0001), (1\(\bar{1}\)0 00), and (112 0), of ZnO are investigated with angle-resolved polarized Raman spectroscopy. The polarization direction dependences of the main Raman peaks are characterized and related to the experimental vibrational modes in the crystal lattice and corroborated by density functional theory (DFT) calculations using two different hybrid functionals. By exploiting the symmetry of the modes and differences in Raman intensity of the optically activated phonons, a simple model is derived for determining the relation between the polar and non-polar crystal orientation. The results are generalized to allow peak intensity ratio analysis using Raman spectroscopy with a non-polarized light source, making it compatible with Raman mapping, as well as to include a critical discussion on the ability to determine the crystal plane orientation and exposed crystal facets using this model for nanodimensional ZnO and equivalent models for other nanomaterials. As the approach allows for use of non-polarized light sources, near-field excitations and local plasmons can in an extension be utilized for the determination of crystal orientation and exposed planes in dimensions much smaller than the diffraction limit.

KEYWORDS
crystal orientation, DFT, Raman spectroscopy, ZnO
1 | INTRODUCTION

Zinc oxide (ZnO) is an abundant and inexpensive semiconductor material. It has been widely studied and used in a variety of technical applications such as LEDs,[1-8] ultraviolet (UV) photodetectors,[11] photocatalysis,[9-14] sun protective cream,[15] paint pigments,[16] and piezoelectrics.[17,18] The optical properties of ZnO are size dependent in the quantum confined region.[19-23] In practical applications, different crystal orientations and facets of the ZnO crystals can be exposed, which translates to different properties: change in polarity, work function, defect density, and surface chemical properties. In general, it is therefore of utmost importance to determine the growth orientations and exposed facets that are present in a nanomaterial. Due to the nanoscale dimensions, however, it has been proven difficult to quantify the facet distribution of nanomaterials. Crystal orientation can be analyzed with several different analysis techniques. High-resolution electron diffraction is suitable for measuring selective sample spots in the low nanometer range, and low-energy electron diffraction (LEED), small-angle X-ray diffraction (XRD), and XRD rocking curves can be used on centimeter- to millimeter-sized samples. However, measuring crystal orientation in the sub-micrometer to micrometer range is experimentally challenging. Electron microscopy and selective diffraction, which today are standard techniques, can successfully measure atomic-scale structures of nanomaterials[24] but is rather elaborate and requires dedicated sample preparation.[25] Therefore, simpler methods, requiring little, or no, sample preparation are desirable to assess crystal orientation of crystals in the 100- to 1000-nm-size range. Crystal growth of metal oxides[26-28] and inorganic–organic materials[29,30] can conveniently be studied with Raman spectroscopy. Detailed interpretations of the local orientation of crystal planes, however, require that full assignments of vibrations and their orientation dependence have been obtained previously, as imperfect crystals and surface states in growing particles can complicate the situation.

In this study, we analyze the orientation-dependent vibrational properties of ZnO single crystals with different crystal orientations using high-resolution Raman spectroscopy. Raman spectroscopy has previously been used to study orientations of crystals in specific orthorhombic[31,32] and tetragonal[33] materials. A thorough work has been done on the 2-D material black phosphorous, where a method based on Raman tensors is suggested to determine the in-plane orientation.[31] However, the method requires rotation of the sample (or laser polarization direction) and is therefore only suitable for single crystals or sheets, and we believe that there is a need for simpler methods compatible with mapping also on poly crystalline materials to endorse wide spread use. Orientation-dependent Raman spectra of three representative hexagonal wurtzite ZnO single crystals are here analyzed in detail to devise a method that faithfully can be used to determine the crystal orientation on the sub-micrometer and micrometer scale, thus bridging the gap between X-ray and electron diffraction. From the results, we derive a simple method without polarization requirements to determine whether polar or non-polar orientations are dominating the exposed crystal structures for thin films and a subsequent discussion how this can be utilized for micromaterials and nanomaterials in general.

ZnO can form three different crystal structures: the hexagonal wurtzite structure, the cubic zinc blende structure, and the cubic rock salt structure.[34,35] In this study, we have focused on the wurtzite structure because it is thermodynamically stable at ambient temperature and pressure. The wurtzite structure of ZnO is shown in Figure 1a, visualized by the software Vesta.[36] Three crystal planes have been included in this study: the polar (0001), also called the c-plane or the basal plane; the non-polar (11 00), also called the m-plane; and the non-polar (112 0), also called the a-plane. These three planes are low energy planes likely to form during crystal growth[37], and in a polar medium, (001) is the most active surface for ZnO crystal growth. The three planes are orthogonal to each other providing a basis set that can be used to parameterize the orientation of the system and span the full space, which ensures that no Raman modes are missed. A projection of the crystal structure along the [0001] axis illustrating the different crystal directions is shown in Figure 1b.

2 | MATERIALS AND METHODS

2.1 | Material (crystals)

Commercially available single crystals were purchased from MTI Corporation. The crystals were 5 × 5 × 0.5 mm, the purity was 99.99%, and the polished surface corresponded to the defined crystal planes (0001), (11 00), and (112 0) with an accuracy of 0.5°, as independently verified by XRD; see Figure S1. The surface roughness was less than 5 Å.

2.2 | Raman spectroscopy

Polarized Raman spectroscopy measurements were carried out on a Renishaw Invia Reflex micro Raman
spectrometer with a 1024 pixel Rencam CCD using a 532-nm excitation laser with plane polarized light, a 2400 lines per millimeter grating and a 50X objective with NA 0.75. The absolute spectral resolution was 1.7 cm\(^{-1}\), and the internal relative accuracy was determined to 0.12 cm\(^{-1}\) by calibration with the reference line of 520.5 cm\(^{-1}\) on a single crystal Si reference for each batch of measurements. The laser power at the sample position was measured to 38.5 mW using a Thorlabs PM160T laser power meter. The use of a relatively high laser power results in high intensity, low noise spectra, and these were compared to low power measurements to rule out laser-induced damage to the samples. The laser light illuminated the surface from a direction along the surface normal. The polarization direction of the incoming laser was fixed throughout the experiment, and the polarization analyzer was set to parallel. The single crystal samples were rotated clockwise azimuthally in 5\(^{\circ}\) steps from 0\(^{\circ}\) to 180\(^{\circ}\) rotation around the surface normal, and data were collected for 30 s for all measurements. For high count spectra, the measurement was divided into two accumulations of 15 s to avoid saturation of the CCD. The geometry of the Raman experiments was as follows: The 0\(^{\circ}\) azimuthal angle \(\Phi\) of the (0001) crystal measurement corresponded to the polarization of the laser being parallel to the [1120] axis. For both the (1100) and the (1120) crystals, the 0\(^{\circ}\) azimuthal angle \(\Phi\) corresponded to the laser polarization direction being parallel to the [0001] axis. Supplementary Raman measurements were done on a different Raman system (Renishaw Invia Reflex) with an Eclipse\(^{\text{TM}}\) filter with a low wave number cut off of 15 cm\(^{-1}\) from the laser. The detector model, laser wavelength and power, and grating line density were identical on the two systems, and data were acquired for six accumulations of 5s for each spectrum.

2.3 | X-ray diffraction

XRD was performed using a Siemens D5000 X-ray diffractometer with Bragg–Brentano geometry, using a Cu K\(\alpha\) X-ray source (\(\lambda = 1.5418\) Å). \(\theta\)-2\(\theta\) scans were done from 20\(^{\circ}\) to 80\(^{\circ}\) angle employing a step size of 0.025\(^{\circ}\), and an acquisition time of 2 s per step was used. The divergence and anti-scattering slits were varied so that the illumination length was 3 mm, constant throughout the scan.

2.4 | DFT calculations

Crystal1\(^{[38,39]}\) was used for calculating the theoretical Raman spectra. The experimental wurtzite ZnO crystal lattice parameters were utilized as a starting geometry and fully optimized with respect to both cell parameters and atomic coordinates using two different hybrid functionals: B3LYP and PBE0 with a 15% Hartree–Fock contribution. Brillouin zone sampling was carried out using a 6 \(\times\) 6 \(\times\) 6 Monkhorst-Pack grid (MPG) for both the optimization procedure and linear response approach. A convergence level of 10\(^{-10}\) Hartree was applied to meet the higher accuracy needed for the subsequent linear response density functional theory (DFT) to obtain the theoretical Raman vibrations. As the regular calculation only generates the transverse optical (TO) frequencies, the longitudinal optical (LO) frequencies were obtained by calculating the
theoretical dielectric tensor with the two functionals and performing subsequent LO–TO split calculations.

3 | RESULTS AND DISCUSSION

The Raman spectra reveal three distinct peaks located at 99-, 332-, and 438-cm\(^{-1}\) Raman shifts present for all crystals. For the non-polar (11 00) and (112 0) crystals, two additional distinct peaks are observed: at 378- and 410 cm\(^{-1}\). The former peak is absent, while the 410 cm\(^{-1}\) peak is present but weak for (0001) cut crystals. Raman spectra for the three crystals are shown in Figure 2. Table 1 shows the mode assignments and corresponding peak positions of the measured and calculated vibrational modes for all peaks, strong and weak, along with their relative intensities at different azimuthal angle \(\Phi\), roughly classified from the experimental spectra (Figures 2 and 3). No Raman peaks with Stokes shift smaller than 99 cm\(^{-1}\) were detected.

From the polarized Raman experiment, it was evident that both the (11 00) and (112 0) crystals showed a large polarization direction dependence whereas the (0001) crystal revealed no polarization dependence at all for the major peaks. The polarization dependences for the major peaks are shown in Figure 3. This graph corresponds to experimentally obtained Raman tensors.

The Raman spectra can be understood from our DFT calculations. First, we note that the absence of the 378 cm\(^{-1}\) peak for (0001) is due to that it originates from the \(A_1\) vibrational mode, which is a non-degenerate mode that vibrates only along the [0001] direction, that is, along the surface normal, and is thus not detectable for plane polarized light parallel to the [0001] axis.

Returning to Figure 3, it can be seen that the azimuthal polarization dependence of the two non-polar (11 00) and (112 0) crystals are very similar. In fact, the only difference is a 13\%–15\% higher intensity count for (112 0), measured as integrated intensity of curve fitted peaks. This means that Raman is an appropriate tool for differentiating between the polar (0001) and the non-polar directions but unsuitable for differentiating the different non-polar crystal directions. This is a disadvantage compared to XRD; see Figure S1a–c that can discriminate between all three. The advantage with a micro-Raman

![Figure 2](https://example.com/image2.png)

**Figure 2** Raman spectra of ZnO (0001), (11 00), and (112 0) crystals. The spectra shown were measured using an azimuthal angle of 45° to clearly display all major peaks. The main peaks are denoted in the spectra. Weak peaks are listed in Table 1 [Colour figure can be viewed at wileyonlinelibrary.com]
system is instead the range of spatial resolution that can be obtained from around 1 µm to millimeters and, if tip-enhanced Raman spectroscopy (TERS) is used, some tens of nanometers. Other advantages of using Raman is its compatibility with mapping and the few restrictions that apply to the samples that even can be measured in

| Peak position, experimental (cm\(^{-1}\)) | Mode assignment | Peak position, DFT-B3LYP (cm\(^{-1}\)) | Peak position, DFT-PBE0 (cm\(^{-1}\)) | Intensity (0001) | Intensity (11 00) | Intensity (112 0) |
|-----------------------------------------|-----------------|----------------------------------------|---------------------------------------|-----------------|-----------------|-----------------|
| 99                                      | E\(_2\) (low)   | 103                                    | 101                                   | 0\(^\circ\)      | -               | 0\(^\circ\)      |
|                                         |                 |                                        |                                       | 45\(^\circ\)     | s               | 45\(^\circ\)     |
|                                         |                 |                                        |                                       | 90\(^\circ\)     | vs              | 90\(^\circ\)     |
| 203                                     | 2 E\(_2\) (low) | 206                                    | 202                                   | 0\(^\circ\)      | w               | 0\(^\circ\)      |
|                                         |                 |                                        |                                       | 45\(^\circ\)     | w               | 45\(^\circ\)     |
|                                         |                 |                                        |                                       | 90\(^\circ\)     | w               | 90\(^\circ\)     |
| 332                                     | E\(_2\) (high) - E\(_2\) (low) | 332                                   | 358                                   | 0\(^\circ\)      | m               | 0\(^\circ\)      |
|                                         |                 |                                        |                                       | 45\(^\circ\)     | w               | 45\(^\circ\)     |
|                                         |                 |                                        |                                       | 90\(^\circ\)     | m               | 90\(^\circ\)     |
| 378                                     | A\(_1\) (TO)    | 386                                    | 403                                   | 0\(^\circ\)      | s               | 0\(^\circ\)      |
|                                         |                 |                                        |                                       | 45\(^\circ\)     | m               | 45\(^\circ\)     |
|                                         |                 |                                        |                                       | 90\(^\circ\)     | s               | 90\(^\circ\)     |
| 410                                     | E\(_1\) (TO)    | 411                                    | 433                                   | 0\(^\circ\)      | -               | 0\(^\circ\)      |
|                                         |                 |                                        |                                       | 45\(^\circ\)     | w               | 45\(^\circ\)     |
|                                         |                 |                                        |                                       | 90\(^\circ\)     | -               | 90\(^\circ\)     |
| 438                                     | E\(_2\) (high)  | 435                                    | 459                                   | 0\(^\circ\)      | -               | 0\(^\circ\)      |
|                                         |                 |                                        |                                       | 45\(^\circ\)     | s               | 45\(^\circ\)     |
|                                         |                 |                                        |                                       | 90\(^\circ\)     | vs              | 90\(^\circ\)     |
| 538                                     | E\(_2\) (high) + E\(_2\) (low) | 538                                   | 560                                   | 0\(^\circ\)      | w               | 0\(^\circ\)      |
|                                         |                 |                                        |                                       | 45\(^\circ\)     | w               | 45\(^\circ\)     |
|                                         |                 |                                        |                                       | 90\(^\circ\)     | w               | 90\(^\circ\)     |
| 589                                     | A\(_1\) (LO)    | 593                                    | 610                                   | 0\(^\circ\)      | w               | 0\(^\circ\)      |
|                                         |                 |                                        |                                       | 45\(^\circ\)     | w               | 45\(^\circ\)     |
|                                         |                 |                                        |                                       | 90\(^\circ\)     | -               | 90\(^\circ\)     |
| 616                                     | E\(_1\) (LO)    | 603                                    | 624                                   | 0\(^\circ\)      | -               | 0\(^\circ\)      |
|                                         |                 |                                        |                                       | 45\(^\circ\)     | -               | 45\(^\circ\)     |
|                                         |                 |                                        |                                       | 90\(^\circ\)     | w               | 90\(^\circ\)     |
| 660                                     | Not assigned    | -                                      | -                                     | 0\(^\circ\)      | w               | 0\(^\circ\)      |
|                                         |                 |                                        |                                       | 45\(^\circ\)     | w               | 45\(^\circ\)     |
|                                         |                 |                                        |                                       | 90\(^\circ\)     | w               | 90\(^\circ\)     |
| 1103                                    | 2 (E\(_2\) (high) + E\(_2\) (low)) | 1076                                  | 1120                                  | 0\(^\circ\)      | w               | 0\(^\circ\)      |
|                                         |                 |                                        |                                       | 45\(^\circ\)     | w               | 45\(^\circ\)     |
|                                         |                 |                                        |                                       | 90\(^\circ\)     | w               | 90\(^\circ\)     |
| 1157\(^a\)                              | 2 A\(_1\) (LO)  | 1186                                   | 1220                                  | 0\(^\circ\)      | m               | 0\(^\circ\)      |
|                                         |                 |                                        |                                       | 45\(^\circ\)     | m               | 45\(^\circ\)     |
|                                         |                 |                                        |                                       | 90\(^\circ\)     | w               | 90\(^\circ\)     |

Abbreviations: DFT, density functional theory; LO, longitudinal optical; TO, transverse optical.

\(^a\)Center position shifts by sample rotation angle. 0\(^\circ\): 1148 cm\(^{-1}\), 45\(^\circ\): 1151 cm\(^{-1}\), 90\(^\circ\): 1157 cm\(^{-1}\).
solution. Usually, there is no need for sample preparation and Raman is suitable for measuring directly on or inside devices, and also during device operation, that is, operando Raman spectroscopy.

It is evident that polarized Raman can give information about the orientation of the ZnO crystals. Based on this, one can construct a simple method to quantify the amount of the sample that have orthogonal vibrational modes with respect to the c axis in the materials. By using the relative intensities between a typical non-polar mode ($A_{1}$, 378 cm$^{-1}$) and a typical polar mode ($E_{2}$ (high), 438 cm$^{-1}$), we get a measure of the degree of polarity. Using a peak ratio instead of absolute intensities gives a sturdy method that is independent of intensity fluctuations and makes data taken with different acquisition time and laser power comparable. To be able to exclude
sample rotation and the \( \Phi \) angle dependence of the Raman signal, we propose the use of non-polarized light as the excitation source. This gives an \( \Phi \) angle-averaged Raman spectrum for the sample and saves us from the impracticality of measuring Raman at a large number of azimuthal angles. Most of the lasers used in Raman spectroscopy have plane polarized light output but to change the system to non-plane polarized light is a minor adjustment. One suitable method is to insert a quarter waveplate into the beam path. The light would then become circularly polarized and excite the sample evenly in all directions. Other methods to depolarize light include using Lyot depolarizers, Cornu depolarizers or wedge depolarizers.

A “real sample,” for example, a nanomaterial, will consist of a mixture of different azimuthally oriented crystal planes, and all planes included in the collection volume of the measurement are contributing to the total Raman spectrum. The collection volume of a confocal Raman measurement is dependent on the laser wavelength, the numerical aperture of the objective used, and the spectrometer apertures.\(^{[41]}\) Using an objective with high NA (0.9), the Raman system used in this work can determine the orientation of 3-D objects down to 0.75 \( \mu \text{m} \) laterally and 1.5 \( \mu \text{m} \) in the vertical direction. The depth resolution was determined by z-scanning and is accurate only at the sample surface as the influence of sample refractive index will cause the depth resolution to increase with sampling depth.\(^{[41]}\) To put this into perspective, one can compare with the X-ray-beam penetration depths for the Bragg reflections from the XRD measurements shown in Figure S1a–c, which are 33–73 \( \mu \text{m} \), depending on angle.\(^{[42]}\) The Raman spatial resolution shows that analysis of crystals smaller than the spatial resolution will yield an average value and that the method is not sensitive to surface reconstruction, which occurs at much smaller dimensions. Measurements of microscale and nanoscale materials also have to be performed with much lower laser power than what has been used for the single crystals in this study due to risk of laser induced heating of individual grains which could cause damage to the samples.

Assuming that the fraction of the sample in the collection volume that consists of a certain crystal plane contributes to the total signal by the same fraction of its own pure single-crystal Raman spectrum, it is easy to calculate the Raman spectrum of any sample as a function of crystal orientation. This assumption will be violated only for repetition of a few lattice planes but will on the other hand be valid for resonance Raman measuring modes down to monolayers of 2-D materials.

Using the data from Figure 3 and averaging the signal intensity (peak height) for all directions for each crystal, crystal specific directional average Raman spectra were obtained. These spectra are identical to the spectra that would be obtained if the same samples were exited with non-polarized or circularly polarized light. For ZnO, the polarization Raman dependence and azimuthal angle averaged spectra for the (11 00) and (112 0) facets are very similar, and an average of these two spectra was used to represent an average non-polar crystal direction. A model was constructed where the intensity ratio between the 378- and 438-cm\(^{-1} \) peaks was calculated for different fractions of polar and non-polar crystal planes. This ratio is a crystal direction specific measure that is very similar for the two non-polar directions [11 00] and [112 0] but clearly different for the polar direction [0001]. The model is presented in Figure 5. A high peak intensity ratio indicates that the non-polar crystal direction is dominating, and a low peak intensity ratio indicates that the polar crystal direction is dominating. The error bars shown in Figure 5 indicate the combined standard deviation of the Raman measurements used to construct the model (laser intensity fluctuations, focusing effects) and the error that would come from a non-equal contribution of (11 00) and (112 0) due to the small signal intensity differences between these planes. The model equation

![FIGURE 5 Model curve showing the intensity ratio between the 378- and 438-cm\(^{-1} \) Raman peaks (A\(_1\)/E\(_2\)(high)) as a function of polar plane fraction, using Raman spectroscopy with a non-polarized 532-nm laser for predicting the dominating plane orientation of a crystal sample. The model uncertainty is shown in brackets. The valued for R\(_f\) and R\(_e\) corresponding to random and equal distribution of polar and non-polar planes are marked.](image-url)
derived from the measured data is described by Equation (1):

\[ R(x) = \frac{Ax + B}{Cx + D}, \]

where \( R(x) \) is the intensity ratio between the 378 cm\(^{-1} \) (non-polar A\(_1\) mode) and 438 cm\(^{-1} \) (polar E\(_2\)(high) mode) peaks, \( x \) is the fraction of polar planes, and \( A, B, C, \) and \( D \) are constants with the values: \( A = -1.982, B = 2.356, C = 6.023, \) and \( D = 4.567. \) The constants are calculated from the Raman peak intensities from the pure single crystals according to

\[ A = I_{(0001);A_1} - I_{(1\overline{1}00),(11\overline{2}0);A_1} \]  
\[ B = I_{(1\overline{1}00),(11\overline{2}0);A_1} \]  
\[ C = I_{(0001);E_2(high)} - I_{(1\overline{1}00),(11\overline{2}0);E_2(high)} \]  
\[ D = I_{(1\overline{1}00),(11\overline{2}0);E_2(high)}, \]

where \( I \) denotes peak intensity values and, in the notation, the miller indices refer to the single crystals measured and \( A_1 \) and \( E_2(high) \) refer to the modes of the Raman peaks, as defined above. Note that \( I_{(1\overline{1}00),(11\overline{2}0)} \) is the average intensity for the two non-polar crystals.

The two non-polar crystals have the same polarized Raman behavior, but as the intensities are not exactly the same, they generate slightly different models. In Figure S2, equivalent model curves for the average and extreme cases 0°, 45°, and 90° rotation, of the (1\overline{1} 00) and (11\overline{2} 0) planes, respectively, are shown. These curves can of course also be used, for a specific well-defined system, but are mainly shown to illustrate that the intensity ratio curves for the average (1\overline{1} 00) and (11\overline{2} 0) curves are very close to each other and that the spread of the curves for different orientation directions is large, which is a strong argument to formulate the method for non-polarized light. For sample assessment, we consider

\[ R = \frac{1}{N} \sum_{1}^{N} R \]

\[ \sigma = \sqrt{\frac{\sum_{1}^{N} (R - \bar{R})^{2}}{N}} \]

for \( \bar{R} > R_e \rightarrow \theta = \bar{R} - \sigma - R_e \)  
for \( \bar{R} < R_e \rightarrow \theta = R_e - \sigma - \bar{R} \]

where \( N \) is the number of measurements, \( \bar{R} \) is the measured \( A_1/E_2(high) \) intensity ratio, \( R \) is the mean value of the intensity ratios, \( \sigma \) is the standard deviation, \( R_e \) is the value of the intensity ratio corresponding to equal contribution from polar and non-polar crystal planes, and \( \theta \) is a model parameter. For the ZnO wurtzite system, \( R_e = 0.18. \) To claim that a sample has a preferential orientation, \( \theta \) has to exceed the uncertainty level of the model, which is 0.027 at \( R_e. \) \( \bar{R} \) can then be compared to the model graph, which gives the fraction of polar planes. If better accuracy is required, \( \bar{R} \) can be inserted into Equation (1). As \( \sigma \) is highly dependent on \( N, \) the number of measurements needed will be lower for highly oriented sample and higher for a moderately oriented sample. We recommend to use \( N > 5 \) and that the measurements are done in different areas of the sample to avoid that in-sample variations pass undetected. For analysis of the inhomogeneity of a material, information from each position will instead be kept where a mapping of the orientation can be extracted. It is worth pointing out that a randomly oriented material will not contain equal amounts of polar and non-polar planes but a 1:2 relation due to having one polar direction and two non-polar directions but the model assessment Equations (8) and (9) can still be used for comparison with a random distribution by replacing \( R_e \) with the intensity ratio for a random distribution, \( R_e = 0.26 \) and comparing \( \theta \) with 0.036, which is the model uncertainty at the point \( R_e, \) \( R_e, \) and their corresponding values are shown in Figure 5.

This model should be generally applicable for single crystals, polycrystalline samples, and epitaxial films of wurtzite ZnO. The model also can be used for other crystal directions than the ones used for model generation, but in this case, as the light will excite both the \( A_1 \) and \( E_2(high) \) modes, the intensity ratio will describe the angle of the measured direction compared to the [0001] direction. The interpretation of the results, however, has to be done with some care. The peak intensities are directly dependent on crystal orientation and not on the exposed crystal facets on the sample surfaces, a point that we believe has been overlooked in previous work on using Raman for orientation analysis. \[33\] This means that special consideration has to be taken when interpreting exposed facets of nanomaterials where the exposed surface areas of the sides of the objects account for a large proportion of the total surface area. For nanomaterials with crystals smaller than the sampling volume of the Raman system, the method will give an average of the measured volume. A number of hypothetical sample morphologies are presented in Figure 6, where the excitation light direction is defined to be vertical.

In the case of free-standing ZnO rods growing in the [0001] direction, the fractional surface area of the non-
polar facets will increase with increasing length of the rods but what a Raman measurement would detect is the increasing number of c-planes, which would indicate the direction of the rods. This is exemplified in Figure 6a. We note that the same considerations must also be made in XRD analysis and is not typical for the Raman method proposed here. The same nanorods in a random growth direction, as shown in Figure 6b, would in a measurement yield a much higher signal contribution from the non-polar planes, and the intensity ratio obtained would describe an average direction of the probe volume. A polycrystalline film with a thickness of about 5 μm, with multiple domains with different plane orientations, as shown in Figure 6c, would be an ideal sample for this method and could, if the individual domains are micron-sized, be readily mapped with a Raman system. In this specific case, surface area of the sides of the domains is negligible, and the exposed crystal facets can be determined. Thin films with a thickness less than the Raman z-resolution can also be mapped in the same way, if the substrate is Raman inactive or has a Raman signal that does not overlap with the peaks used for the analysis. This is a useful expansion of the method scope, which is enabled by the use of intensity ratios rather than absolute intensities. Figure 6d–f show single crystals grown in the [0001] direction. The crystal in Figure 6d would of course show a major contribution from the (0001) plane, but the same sample tilted as shown in Figure 6e would give an increased contribution from the non-polar facets. Figure 6f shows a sample where the crystal facet that terminates the surface is different than the crystal growth direction, a situation that will not be detected by this method.

4 | CONCLUSIONS AND FINAL REMARKS

The proposed approach can conveniently be applied to any sample size of ZnO down to sub-micrometer domains and will only be limited by the diffraction limit of the laser used in the Raman spectrometer setup. For planar films, this will allow analysis of exposed crystal planes in sub-micrometer domains. In the vertical direction, a spatial resolution of better than 2 μm can be achieved, but, as mentioned, thinner layers than this can be analyzed if the substrate signal does not interfere. There are several possible approaches to extend the range of the method to even smaller dimensions. The most obvious is to minimize the Abbe diffraction limit, \( d = \frac{\lambda}{2NA} \), which determines the lateral spatial resolution. Here, \( d \) is smallest resolvable distance (almost equal to half the laser spot size), NA is the numerical aperture of the objective in a micro-Raman setup, and \( \lambda \) is the wavelength of the Raman laser. Optimizing \( \lambda \) and objective NA can give a notable improvement. Using a 100X oil immersion objective with NA = 1.4 and a 405-nm Raman laser, this translates to a spatial resolution of 145 nm, which is close to the limit for this approach. Using super sampling,
where the sample stage is moved in smaller steps than laser the spot size is a requirement to achieve this.

For nanomaterials in general, the information obtained would be related to the crystal plane growth orientation and only related to the exposed crystal plane in selective cases as outlined in context to Figure 6. Plane accumulation or crystal domains that are below the diffraction limit can instead be approached by using tip-enhanced Raman spectroscopy (TERS) where a local plasmon field down to 10 nm can be achieved or by using near-field optical microscopy (SNOM) Raman, although at the expense of convenience and Raman signal. There are also other challenges when measuring properties of very small nanoparticles. Assuming that the diffraction limit can be overcome with tip-enhanced or near-field approaches, some of the Raman modes can be suppressed as the dimension approaches the optically quantum confined region, and models based on bulk properties need to be modified to incorporate vibrational changes from the material’s low dimensionality. In addition, due to the low intensity expected from the local excitation and collecting the Raman scattering in far field, near resonance, or resonance Raman where the Raman scattering is collected at near or full band gap excitations, are convenient options. As the dimension approaches the optically quantum confined region, however, the band gap increases with respect to the bulk band gap and the wavelength for resonance Raman changes for the material at hand. The limit for the optically quantum confined region is fairly well defined as the exciton Bohr radius, which usually is used to define this, has for wurtzite ZnO been reported from 2 nm, but this limit has to be taken with some caution because according to theoretical models and experimental work the optical band gap is significantly increased for particles up to as large as 8 nm in diameter and vibrational confinement beyond 10 nm For local analysis of bulk material, this is not a concern, but for low-dimensional materials approaching the exciton Bohr radius in the material, both vibrational and electronic quantum confinement have to be taken into account, affecting both the intensities and available phonon modes. Finally, we point out that the same approach can be used to derive the non-polarized Raman intensity ratios and thus orientation information for other material systems that exhibit crystal direction dependent Raman spectra.

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