I. INTRODUCTION

Interest in semiconductor nanowires (NWs) is driven by the promise of miniaturized high-density electronics, optoelectronic devices, such as light emitters, polarization-sensitive photo-detectors, and photo-transistors as well as for their use in flexible electronics. Materials in NW form can exhibit crystal structures which do not occur in the bulk. For example, due to the nucleation mechanisms involved in the growth of GaAs NWs, they can crystallize into the wurtzite (WZ) structure, although GaAs otherwise always crystallizes in the zincblende (ZB) structure. Depending on the growth conditions, there can also be both ZB and WZ crystalline phases in the same GaAs NW. If these phases exhibit different energy gaps, there will be a potential band for carriers in the conduction band (CB) and valence band (VB) at the WZ/ZB interface. NWs with mixed WZ and ZB phases can therefore offer interesting possibilities, such as quantum confinement along the NW axis through the formation of quantum discs or superlattices, which can be useful for novel device applications, including efficient light-emitting diodes and lasers. An understanding of the electronic band structure (EBS) and emission properties of mixed-phase NWs is therefore important for the design of such devices.

The energy gap of ZB GaAs $E_{g}^{ZB}$ is 1.519 eV at low temperatures and 1.424 eV at room temperature, but there are conflicting reports regarding the energy gap of ZB GaAs $E_{g}^{ZB}$. Based on different experimental techniques and theoretical models, values of $E_{g}^{ZB}$ ranging from 20 meV below and up to 100 meV above the value of $E_{g}^{ZB}$ have been reported, which are listed in the first column of Table I. WZ GaAs is also expected to have a non-zero crystal field energy parameter $\Delta_{cr}$, which results in a splitting $\Delta E_{lh-hh}$ of the heavy-hole (hh) and light-hole (lh) VBs. Theoretically predicted and experimentally determined values of $\Delta_{cr}$ are compiled in the second column of Table I, vary from 122 to 197 meV. Similarly, the experimentally determined values of $\Delta E_{lh-hh}$ listed in the third column of Table I also cover a large range from 16 to 103 meV. The band alignment between the ZB and WZ sections is another important issue for mixed-phase NWs. There is an agreement that the alignment is of type-II with the VB top of WZ GaAs lying above that of ZB GaAs.

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<table>
<thead>
<tr>
<th>$E_{g}^{WZ} - E_{g}^{ZB}$ (meV)</th>
<th>$\Delta_{cr}$ (meV)</th>
<th>$\Delta E_{lh-hh}$ (meV)</th>
</tr>
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<tbody>
<tr>
<td>0: LT-PLS (Ref. 7)</td>
<td>122: Theory (Ref. 19)</td>
<td>16: LT-PLS (Ref. 21)</td>
</tr>
<tr>
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<td>129: Theory (Ref. 13)</td>
<td>65: RT-RRS (Ref. 14)</td>
</tr>
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<td>186: Theory (Ref. 20)</td>
<td>90: LT-PCs (Ref. 11)</td>
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<tr>
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<td>189: LT-RRS (Ref. 10)</td>
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<tr>
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<tr>
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<tr>
<td>32: Theory (Ref. 13)</td>
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<tr>
<td>35: RT-RRS (Refs. 14 and 15)</td>
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<tr>
<td>55: RT-CLS (Ref. 17)</td>
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<tr>
<td>100: RT-TM (Ref. 18)</td>
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lowest energy transitions will be spatially indirect. Spirkoska et al.\textsuperscript{21} have reported a polarization resolved microphotoluminescence (\(\mu\)-PL) study of spatially indirect transitions in mixed-phase NWs under low excitation intensities and estimated \(\Delta E_{hhl}\) to be about 16 meV, which is significantly smaller than the other values listed in Table I. In order to probe these discrepancies, we have performed a \(\mu\)-PL study on such mixed-phase NWs using a different excitation scheme than in Ref. 21, i.e., exciting the whole NW at a time and using both low and high excitation intensities. This enabled us to observe spatially direct transitions in such NWs. The observed emission characteristics are further analyzed by a comparison with results of calculations based on \(k \cdot p\) perturbation theory.

II. EXPERIMENTAL DETAILS

The GaAs NWs were grown by molecular beam epitaxy using Ga-induced vapor-liquid-solid growth on phosphorus-doped Si(111) substrates. A thin shell of Al\(_0.1\)Ga\(_0.9\)As was grown around the NWs to minimize GaAs surface states and thereby enhance the luminescence efficiency. Electron microscopy images,\textsuperscript{17} an example of which is shown in Fig. 1, demonstrate that the NWs have an average diameter of 150 nm and a length of 8 \(\mu\)m. Investigations\textsuperscript{17} with high-resolution x-ray diffraction and Raman spectroscopy indicated the presence of both WZ and ZB sections along the axis of these NWs. \(\mu\)-PL spectroscopy was performed on broken off, single NWs dispersed on a Au-coated Si substrate, which was placed on the sample stage of a liquid-He cryostat and cooled to 4.5 K. The NWs were excited with the 632 nm line of an unpolarized He-Ne laser. A 0.55 m focal length monochromator (MC) was used to spectrally disperse the luminescence. The PL signal was subsequently detected with a Peltier-cooled Si charge coupled device (CCD). During the measurements, a NW was imaged on the entrance slit of the MC using optics that included a long-working-distance objective (magnification of 100\(\times\) and numerical aperture NA of 0.5), which also collects the PL emission. The substrate was oriented in such a way that the image of a NW on the MC slit was aligned with its axis parallel to the entrance slit, and an entire NW could then be observed on the CCD under white light illumination. For recording such images, the MC grating was set to the zero-order position making it act like a plane mirror. Such a diffraction-limited image of a NW is shown in Fig. 2(a). By using an extra lens in the path of the laser, the laser spot on the sample was defocused so that the entire NW was excited. With this arrangement, the measured values from a row of pixels on the CCD correspond to the emission spectrum from a specific section along the axis of the NW with a spatial resolution of 1.5 \(\mu\)m. This enabled us to measure spatially resolved PL spectral images of the NWs. The polarization of the emitted PL signal was separated into components parallel (\(\parallel\)) and perpendicular (\(\perp\)) to the NW axis using a Glan-Thomson polarizer placed in front of the MC. The polarization directions parallel and perpendicular to the NW axis also coincide with the two eigen polarization directions of our setup, which are parallel and perpendicular to the MC slits. The spectral

![FIG. 1. The scanning electron microscope image of the NWs shows a hexagonal cross-section indicating growth along the direction [111] in case of the ZB and the e-axis [0001] in case of the WZ crystal phase.](image)

![FIG. 2. (a) Diffraction-limited image of a GaAs NW under white light illumination recorded through the MC input slit. Spectrally dispersed \(\mu\)-PL images of the NW for PL polarization (b) E \(\perp z\) and (c) E \(\parallel z\). The pixels along the vertical direction represent the position along the NW axis. In images (b) and (c), pixels along the horizontal direction are correlated with the emitted photon energy and have been transformed accordingly. The sample stage temperature and excitation intensity were 4.5 K and 1.8 kW/cm\(^2\), respectively. In (b) and (c), the \(\mu\)-PL signal strength (scale bar on top) is shown on a logarithmic scale.](image)

![FIG. 3. Polarization resolved \(\mu\)-PL spectra from (a) region (i) and (b) region (ii) of the GaAs NW shown in Fig. 2 with the PL intensity displayed on a logarithmic scale. The spectra are shown for polarization directions E \(\perp z\) and E \(\parallel z\) at low (5.6 W/cm\(^2\)) and high (1.8 kW/cm\(^2\)) excitation intensities. The dashed line in (a) indicates the slope of the high-energy tail of the PL spectrum.](image)
response of our setup for these two polarization directions was separately measured and used to correct the measured polarized PL spectra.

III. RESULTS AND DISCUSSION

The \( \mu \)-PL spectral images of the NW in Fig. 2(a) with the intensity plotted on a logarithmic scale are shown in Figs. 2(b) and 2(c) for PL polarization \( E \perp z \) and \( E \parallel z \), respectively. The images are representative for the data obtained from 18 different NWs. Here, \( z \) denotes the direction along the NW axis, corresponding to the [111] direction for ZB and the \( c \)-axis for WZ sections. The variation along the \( z \)-direction represents emission from different regions along the NW axis. Previous results using cathodoluminescence spectroscopy and imaging\(^{17}\) have also shown similar regions of strong emission along the NW axis at different energies, but these measurements could not determine their polarization characteristics. We have marked two such regions in Fig. 2 by dashed horizontal lines showing strongly (i) and weakly (ii) polarized PL emission. Note that the strongly polarized PL peak in region (i) occurs at higher energies.

The PL spectra from regions (i) and (ii) marked in Fig. 2 for two different excitation intensities are shown in Figs. 3(a) and 3(b), respectively. The lower excitation intensity of 5.6 W/cm\(^2\) was just sufficient to observe PL signals for both polarization directions, while for the higher value of 1.8 kW/cm\(^2\) the low-energy spectral features were already saturated. For the low excitation intensity, the PL intensity exhibits sharp spectral features, which are strongly polarized with \( E \perp z \) in both regions (i) and (ii). Such polarized emission for low excitation intensities has already been reported previously.\(^{21}\) However, for high excitation intensities, the PL spectrum evolves into a dominant broadened feature, which in region (i) is stronger for the polarization \( E \perp z \) and peaks at 1.535 eV, while the weaker signal for \( E \parallel z \) peaks at a higher energy around 1.55 eV. In contrast, the PL emission under high excitation in region (ii) is relatively weakly polarized, with the peak intensity occurring around 1.51 eV for \( E \parallel z \). Since the strongly polarized emission in region (i) is more interesting, we have plotted the PL spectra from this region for high excitation intensity in Fig. 4 with the PL intensity on a linear scale. Note that in comparison to the spectral feature for \( E \parallel z \) the higher intensity spectral feature for \( E \perp z \), which occurs at a lower energy, is also broader.

Emission from unstrained ZB GaAs is expected to be unpolarized.\(^{25}\) However, the VB structure of a WZ crystal is such that it can result in polarized emission.\(^{26}\) Our results can therefore be understood by considering the two scenarios displayed in Figs. 5(a) and 5(b), which show the energy band diagram along the NW axis having WZ- and ZB-dominated regions, respectively. Transmission electron microscopy data on other samples of this type have given evidence for the presence of such regions.\(^{21,23}\) Photoexcited electrons (holes) would quickly diffuse\(^{22}\) into the CB (VB) potential wells of the ZB (WZ) sections. Regions along the NW, which contain several adjacent electron and hole wells, have a higher probability of radiative recombination, which results in spatially localized emission. For low excitation intensities, the wells would be partially filled with electrons residing in the ZB regions and holes in the WZ regions, and these carriers would radiatively recombine through spatially indirect transitions (labeled \( T_{\text{SI}} \)\(^{17,21,23}\)). Such transitions give rise to the sharp features for low excitation intensities in Figs. 3(a) and 3(b) and have been analyzed previously taking into account the potential profile at a WZ/ZB interface.\(^{17}\) The predominantly \( E \perp z \) polarization of these sharp transitions occurs because they involve the lower energy \( hh \) states in the WZ section, whose wavefunction does not have a \( p_z \) atomic orbital component.\(^{21}\) The weak signal present for \( E \parallel z \) may be due to a combination of geometry, optics, and strain effects, which will be discussed in more detail below. The distribution of the emission energies of these sharp features may arise from the differences in the confinement energies due to the different widths of the WZ and ZB sections. Some
features could also involve transitions between a confined electron/hole and an acceptor/donor-like defect level, which can have a similar polarization characteristic as long as the defect levels are shallow.\(^{27}\)

Next, consider the net potential barrier \(\Delta E_x\) and \(\Delta E_y\) experienced by the confined electrons and holes, respectively. Figure 5(a) indicates that \(\Delta E_x + T_{SI} - \delta_E = E_{nWZ}^Z\), where \(\delta_E\) is the hole confinement energy. Since we will argue later that the value of 1.535 eV corresponds to the average energy gap of the highly luminescent regions in the WZ-dominated sections, we will now assume that the low temperature (LT) \(E_{nWZ}^Z\) is close to 1.535 eV. However, this value does not represent the energy gap of pure WZ GaAs. Furthermore, the energy of the strongest spatially indirect transition for low excitation intensities in Fig. 3, which is expected to correspond to the majority of the indirect transition for low excitation intensities in Fig. 3, GaAs. Furthermore, the energy of the strongest spatially indirect transition for low excitation intensities is not itself indicates that the cumulative effect of these phenomena on the emission polarization characteristics is not significant.

Using a similar line of argument as above, we identify the strongly polarized emission observed for high excitation intensities in region (i) of the NW in Figs. 2, 3(a), and 4 as arising from spatially direct \(T_{SD}\) transitions in the WZ-dominated sections of the NW. Note that this emission cannot originate from the Al\(_{0.1}\)Ga\(_{0.9}\)As shell, because it exhibits a much larger LT energy gap of 1.64 eV. The dominant PL feature from region (i), which peaks at 1.535 eV for \(E_{\perp z}\) as shown in Fig. 4, is attributed to transitions predominantly involving hh states, which we will verify below. The emission for \(E_{\parallel z}\) peaking at 1.55 eV is attributed to transitions involving lh states. This polarization anisotropy here is much stronger and different compared to the anisotropy seen in the ZB-dominated regions. We attribute the observed shift of 15 meV as occurring mainly due to crystal-field induced splitting \(\Delta E_{lh-hh}\). The decrease in the PL signal at higher emission energies \(E\) can be approximated by \(\exp\left[-E/(k_BT_c)\right]\), where \(k_BT_c\) denotes the Boltzmann constant and \(T_c\) an effective carrier temperature. From the slope of the PL spectrum at high energies in Fig. 3(a), we obtain \(T_c = 94\) K, for which \(k_BT_c = 8.2\) meV. This effective carrier temperature is likely to be a consequence of the high excitation intensity and explains how the higher-energy lh states can be populated. The characteristics of polarized PL emission from all the NWs studied are summarized in the inset of Fig. 4, which displays the difference in the emission peak energies for \(E_{\parallel z}\) and \(E_{\perp z}\) polarizations. This difference identified as \(\Delta E_{lh-hh}\) is plotted as a function of the energy of the \(E_{\perp z}\) emission peak.

For a further analysis, we determined the EBS of WZ GaAs using \(\mathbf{k} \cdot \mathbf{p}\) perturbation theory.\(^{26}\) We calculated the relative oscillator strength components \(f_x, f_y, \) and \(f_z\) (i.e., hh, lh) of the transitions,\(^{30}\) which determine the relative emission intensity for polarization parallel to the \(x, y,\) and \(z\) directions, respectively. The spin-orbit energy parameter \(\Delta_{cr}\) is expected to be the same\(^{13}\) in WZ and ZB GaAs and was taken to be 348 meV. The main difference between the ZB and WZ GaAs band structure at the \(\Gamma\) point arises from the non-zero crystal field energy parameter \(\Delta_c\) for the latter. In Fig. 5(c), we display \(\Delta E_{lh-hh}\) as a function of \(\Delta_{cr}\). The inset shows a schematic of the relevant bands involved in these transitions. In the limiting case of \(\Delta_{cr} = 0\), we obtain \(\Delta E_{lh-hh} = 0\) as expected in ZB GaAs. From Fig. 5(c), we obtain for \(\Delta E_{lh-hh} = 15\) meV a value of \(\Delta_{cr} \approx 23\) meV. In Fig. 5(d), we show the variation of the oscillator strength components of the two transitions as a function of \(\Delta_{cr}\). We see that for the hh transition \(f_{hh}^f = f_{x}^{f_{hh}} = 0.5\) and \(f_{yy}^{f_{hh}} = 0\), while for the hh transition \(f_{xx}^{f_{hh}} = f_{yy}^{f_{hh}} = 0.5\). In general, they follow the sum rule \(\sum_{j=x,y,z} f_{jj}^{f_{hh}} = 1\), where \(i=x, y, z\) and \(j=hh\) or lh. It is not possible to directly compare these calculated \(f_i\) values with the measured emission intensities for \(E_{\parallel z}\) and \(E_{\perp z}\) polarization since the joint density of states also needs to be taken into account. Also the shift in the transition energy brings in additional factors involving the effective carrier temperature and relative occupation of the hh and lh bands. However, we can compare the oscillator strength of the hh transition itself for the two polarization directions. For \(\Delta_{cr} = 23\) meV, the results in Fig. 5(d) indicate that the lh-related emission for \(E_{\parallel z}\) is expected to be stronger than for \(E_{\perp z}\) with a ratio \(f_{hh}^{f_{lh}}/f_{hh}^{f_{hh}} \approx 3.6/1\). We have fitted Gaussian lineshapes to the dominant spectral features in Fig. 4. The small spectral feature at lower energies has been neglected for each
polarization direction. These transitions are likely due to saturated $T_{nl}$ and impurity- or defect-related transitions.\cite{17} For the broader feature for $E_{1Lz}$, we used two Gaussian lines peaked at about 1.535 eV (hh transition) and 1.55 eV (lh transition). Only one Gaussian line was used for $E_{1Lz}$ peaked at about 1.55 eV (lh transition). The full width at half maximum amounts to 23 meV for all three lines. We find that the ratio of the area of the lh contribution for the $E_{1Lz}$ and $E_{1Lz}$ polarized PL emission is about 3.2/1, which is close to the calculated ratio given above. It is also evident from the fits that the lh contribution to the $E_{1Lz}$ polarized PL emission is negligible, which is what one expects for $f_{lh}^D = 0$.

The inset of Fig. 4 shows a distribution of the $\Delta E_{lh-hh}$ values and of the emission peak energy values for $E_{1Lz}$ for the WZ-dominated regions with average values of 13 meV and 1.535 eV, respectively. Our results therefore might seem to suggest an average $\Delta E$ and LT $E_{lh}^{WZ}$ value close to 20 meV and 1.535 eV, respectively. However, this $\Delta E$ value is much smaller than the theoretical predictions for WZ GaAs.\cite{13,19,20} These $\Delta E$ and $E_{lh}^{WZ}$ values are also smaller than experimentally determined values based on resonant Raman spectroscopy (RRS) (Ref. 14) and PL (Ref. 16) studies on WZ NWs with high phase purity. In contrast, our $\Delta E$ value is close to the value of 16 meV obtained by Spirkoska et al.,\cite{21} who also worked with WZ-ZB mixed-phase NWs. A possible explanation for the low values in mixed-phase NWs could be the following. It has been suggested that due to twinning the hexagonality of regions around the WZ section in such WZ-ZB mixed-phase NWs can be lower than 2H (WZ), such as 4H, 6H, etc.\cite{21} With decreasing hexagonality from 2H to 6H, model calculations\cite{13} have shown that the energy gap decreases by 14 meV, but that $\Delta E$ decreases even more by about 77 meV. In our mixed-phase NWs, one would expect that the photo-generated carriers accumulate in regions with the lowest energy gap after the shallow wells have been filled for high excitation intensities. Therefore, these carriers eventually recombine in regions of lower hexagonality. Consequently, we obtain lower values for the emission peak energy and $\Delta E$, as compared to WZ-phase GaAs NWs with high phase purity. A possible reason for the different reported values of the energy gap of WZ GaAs in mixed-phase NWs could be the presence of such twinned sections of varying type and extent.

IV. CONCLUSIONS

In conclusion, using $\mu$-PL spectroscopy with a modified excitation scheme, we have studied single GaAs NWs that contain sections with WZ and ZB phases. We were able to detect emission due to spatially direct transitions from both WZ- and ZB-dominated regions. Our results support the hypothesis that carriers in the WZ-dominated regions of such mixed-phase NWs tend to diffuse to and recombine in regions that exhibit a lower hexagonality arising from twinning.

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