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Fine optical spectroscopy of the 3.45 eV emission line in GaN nanowires

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GaN nanowires grown by plasma-assisted molecular beam epitaxy are of excellent optical quality, their optical signature being characteristic of homogeneous strain-free GaN. There are however discrepancies between the low temperature luminescence spectra of GaN thin films and nanowires, in particular, a strong emission line around 3.45 eV in nanowires is not found with such a large intensity in thin film GaN. The origin of this emission line in nanowires is still debated; in this article, we shed new light on this debate notably by polarization-resolved luminescence and magneto-luminescence experiments. Our findings demonstrate, in particular, that this line cannot be attributed to a two-electron satellite of the donor bound exciton transition. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4775492]

I. INTRODUCTION

It is now widely recognized that the bottom-up growth of semiconductor nanowires (NWs) allows one to obtain high quality strain-free material in heteroepitaxy. This is particularly remarkable for GaN nanowires grown by plasma-assisted molecular beam epitaxy (PA-MBE)1–3 or by metal-organic vapor phase epitaxy (MOVPE),4 for which low temperature luminescence linewidths of the donor bound exciton (D0X) around a few meV can be obtained for nanowires only a few 100 nm long on a heterosubstrate. In the most studied system, namely GaN nanowires grown by PA-MBE on a silicon substrate, it has been however recognized that the optical spectroscopy5 does not exhibit the same features as what is observed in high quality strain-free thin films.5 In particular a line at around 3.45 eV is observed in most PA-MBE grown nanowire samples in low-temperature (<50 K) photoluminescence (PL) and has been under scrutiny of several groups in the past ten years, as it seems to be specific to these nanowires. The origin of this line is still debated, although several explanations have been put forward to account for this spectral feature. It is the aim of this article to present new optical spectroscopy experiments that allow one to gain more insight into this 3.45 eV emission line.

The low temperature (4 K) PL of ensembles of PA-MBE grown nanowires always exhibits a luminescence line at 3.471 ± 0.001 eV corresponding to the D0X(A) recombination in strain-free GaN. In most samples, a spectral line around 3.45 eV is also observed at low temperature, as discussed in the first study on the optical properties of PA-MBE grown nanowires.3 Its intensity can depend on the growth conditions and possibly on the optical set-up but it is generally of the same order of magnitude as the D0X(A) line. As pointed out in Ref. 3, an emission line around 3.45 eV is usually seen in bulk GaN spectroscopy, identified as the two-electron satellite (TES) of the D0X(A) transition, however, with a very weak intensity about two orders of magnitude lower than the D0X(A) transition.6 In Ref. 3, the 3.45 eV line is tentatively ascribed to an interstitial Ga point defects (GaI) formed in the core of the nanowires. With the wide development of research on nanowires in the recent years, a renewed interest in the spectroscopy of GaN NWs took place. Robins and coworkers have discussed the various sub-band-gap luminescence lines of PA-MBE grown GaN nanowires.7 They show correlations between these lines and the various sub-band-gap luminescence lines observed in GaN thin films. In particular they note that the 3.45 eV line in GaN thin films has been assigned to excitons bound to inversion domain boundaries.8 This attribution in the case of the luminescence of PA-MBE grown nanowires is convincingly refuted in Ref. 9. Furtmayr and coworkers have attributed the 3.45 eV line to a near-surface Ga vacancy (V_{Ga}).10 This is based on the fact that nanowires are grown in N-rich conditions, and that Furtmayr et al. observe a reduction of the relative 3.45 eV contribution for larger III/V ratios. They also report a decrease in the 3.45 eV line intensity in Mg-doped samples, which according to them is consistent with the fact that the formation of the V_{Ga} point defect is favored in n-type GaN. Next a publication dealing explicitly with the 3.45 eV line studied by time-resolved photoluminescence argued that it is a TES with a much enhanced intensity due to donors located near the surface.9 Then Lefebvre et al. coworkers correlated the intensity of the 3.45 eV line with the growth conditions and hence the NW morphology.11 Their conclusion is that the intensity of the 3.45 eV line is larger for low density and small diameter nanowires, thus, confirming that this line is linked to a surface effect. Note
that the correlation of the 3.45 eV line with NW density was already reported in Ref. 3. By studying the PL of single GaN nanowires either dispersed on a silicon substrate or grown at low densities on Si(111) or Si(100) substrates, Brandt, Pfüller, and coworkers have shown that some NWs do not emit at 3.45 eV while for other NWs this emission seems to dominate.\textsuperscript{12,13} They argue in Ref. 12 that the 3.45 eV line should stem from a surface point defect.

We also would like to report on the few articles in which the 3.45 eV line is not seen, or at least not seen with a significant intensity compared to the D0X(A) line. A first trivial remark: as the 3.45 eV line and the D0X(A) line are 20 meV apart, a D0X(A) linewidth at least below 10 meV is required to be able to clearly distinguish both lines. In an article studying polarization properties of single nanowires reported on a sapphire plate, Schlager, Robins, and coworkers have reported PL spectra that do not show any significant peak at 3.45 eV.\textsuperscript{14,15} Aschenbrenner and coworkers have published a PL study of nanowires grown by PA-MBE on GaN islands grown by MOVPE on r-plane sapphire.\textsuperscript{16} Their spectra do not show any peak at 3.45 eV. Finally, Chen and coworkers have shown the spectroscopy of single GaN NWs grown on c-sapphire by MOVPE.\textsuperscript{4} Again, no peak at 3.45 eV is observed in the low temperature PL of these NWs. For the last two examples, the growth is done on sapphire, so that one might wonder whether this might be a reason for the absence of 3.45 eV peak. However, the 3.45 eV line was clearly seen for NWs grown by PA-MBE on c-sapphire in Ref. 3. We still can note that in Refs. 4 and 16, the NWs have diameters in the 100–200 nm range, i.e., quite larger than for most PA-MBE grown NWs found in the literature that have diameters in the 30–50 nm range. This remark might also apply to Refs. 14 and 15 in which quite long (5.7 \(\mu\)m) and quite thick NWs are studied: the NWs diameters are specified to be in the 50–250 nm range in the abstract of Ref. 15. Finally, we note that on single NW spectroscopy of low density samples, Pfüller and coworkers reported that samples grown on Si(001) do not show the 3.45 eV line, while similar samples grown on Si(111) do show this transition. The absence of 3.45 eV line for samples grown on Si(001) can however not be generalized as the same group showed the 3.45 eV line in the PL of ensembles of GaN NWs grown on Si(001)\textsuperscript{17} while another group also clearly observed the 3.45 eV line for GaN NWs grown on Si(001).\textsuperscript{18}

The conclusion we can draw from this literature review is that while several hypothesis have been made concerning the possible origin of the 3.45 eV line, there is still no consensus on this issue. Generally speaking, it can be said that this line appears more strongly in non-coalesced NWs and for thin (diameter < 50 nm) NWs although this is not completely general as for instance Kouyama and coworkers clearly see the 3.45 eV line for nanowires with an average diameter of 150 nm,\textsuperscript{19} however, with an unusually large excitation power in the MW cm\(^{-2}\) range. In this article, we show thanks to new PL experiments that the 3.45 eV line has some unique luminescence properties. These features discard some of the previous interpretations and also limit the number of mechanisms that can be responsible for this emission.

II. SAMPLES AND OPTICAL EXPERIMENTS

To go beyond the current knowledge on the spectroscopy of small diameter (<50 nm) GaN nanowires, we present additional PL experiments in order to probe fundamental properties of the 3.45 eV line. The samples we study are grown by PA-MBE on silicon (111) substrates following the growth procedure described in Ref. 20 (samples A) or by following the growth procedure described in Ref. 21 (samples B and C). Sample A is grown with a thin AlN buffer layer before the NW growth. Samples B and C are grown without AlN buffer layer and at a higher substrate temperature, so that a strong density gradient is obtained along the radius of the two-inch wafer following the substrate temperature gradient.\textsuperscript{21} While samples A and B are nominally undoped, sample C is doped with Mg. In all samples A, B and C the nanowire diameters are in the 30–50 nm range, with slightly smaller diameters (down to 20 nm) in the low density regions of samples B and C. Scanning electron micrographs of sample A and C are shown on Figure 1. The micrograph on sample C is taken in the low density (i.e., high growth temperature) region of the sample, where the nanowires are shorter and with somewhat smaller diameters. Note that the slight Mg doping in sample C has no effect on the nanowire shape; nanowires in samples samples B and C have indeed the same morphologies. MicroPL experiments were performed in a helium flow cryostat, the excitation light is the frequency-doubled beam at 244 nm from an argon laser, the collected luminescence being analyzed by a 550 mm focal length grating spectrometer (1200 or 1800 grooves mm\(^{-1}\)) and detected by a nitrogen cooled Si charge coupled device. The excitation beam was focused onto a ~1 \(\mu\)m spot with a 0.4 numerical aperture microscope objective and the luminescence was collected through the same optics. The microPL signal could be analyzed in linear polarization by

![FIG. 1. Scanning electron micrographs of (a) sample A and (b) sample C in the low density region. Note that nanowires in samples B and C have the same morphology.](Image)
inserting a rotating half-wave plate (in the present case a Berek compensator tuned to act as a half-wave plate at the analyzed wavelength) and a fixed Glan linear polarizer. In case of magneto-PL experiments, which have been performed at the Laboratoire National des Champs Magnétiques Intenses in Grenoble, the sample was directly immersed in a bath of liquid helium. The excitation light came from a helium-cadmium laser emitting at 325 nm and was sent to the sample via a large core (200 µm) optical fiber. The laser beam was shone onto the sample directly at the exit of the optical fiber with a distance between the fiber output and the sample estimated to be around 200 µm. The luminescence was then collected through the same fiber, analyzed by a 50 cm focal length grating spectrometer (3600 grooves mm⁻¹) and detected by a nitrogen cooled Si charge coupled device. The magnetic field was obtained from a resistive coil and could reach 22 T. The sample could be oriented either with the c-axis parallel to the magnetic field (Faraday configuration) or with the magnetic field perpendicular to the c-axis (Voigt configuration). In Faraday configuration, a circular polarizer could be inserted between the optical fiber and the sample. Regular PL spectra were obtained in the same set-up (and without circular polarizer) at zero magnetic field.

III. POLARIZATION RESOLVED PHOTOLUMINESCENCE AND MAGNETO-PHOTOLUMINESCENCE EXPERIMENTS

PA-MBE grown GaN nanowires are in the wurtzite phase, unless peculiar low temperature growth conditions are used. Due to the particular symmetries of the wurtzite structure, the upper valence band splits into three closely lying bands. The transitions of either of these valence bands to the fundamental conduction band have distinctive dipole orientations which translate into linear polarization properties of the emitted photons. The analysis of the linear polarization of the PL of a wurtzite III-N structure thus allows to gain information on the valence bands involved in the optical transitions under study. In order to have more insight into the 3.45 eV transition dipole orientation, we performed a low temperature microPL experiment on a cleaved facet of the nominally undoped sample A (Fig. 2). By focusing the laser on the side of the NWs, it is possible to access the polarization (perpendicular or parallel to the c-axis) of the emitted lines, which allows to distinguish the contributions of the A, B and C excitonic transitions. Not surprisingly, the D0X(A) transition is strongly polarized perpendicularly to the c-axis, as expected for an A-type exciton. We still note that the degree of polarization (defined as $I_{\parallel}/I_{\perp}$) is limited to 0.7. This can be explained by the fact that some nanowires present some inclination with respect to the substrate, and also that the scattering of the emitted light within the nanowire ensembles might somewhat smear out the polarization information. It is however striking to see that the 3.45 eV line is counter polarized with respect to the D0X(A) line, and presents a polarization degree along the c-axis of 0.8. As the TES has essentially the same polarization selection rules as the corresponding D0X transition, this first experiment shows that the 3.45 eV line cannot be a TES linked to a D0X(A) transition. The authors of Ref. 9 attribute the 3.45 eV line to a TES of a surface D0X(A), in which case the wavefunctions of the bound carriers might be different from what they are in the bulk (which can be a qualitative argument to explain the unusually large intensity of the TES transition in NWs). While it is true that the envelope function of the donor bound exciton can be affected by the proximity of the surface, the Bloch wavefunctions which are responsible for the polarization properties of the transitions are essentially unaffected in the framework described by Corfdir and co-workers, so that polarization selection rules should still hold. We also note in Fig. 2 that the lineshape of the 3.45 eV line is exactly the same for both polarizations. This means that if this line is made of several contributions, they all have the same polarization behavior. In particular, this discards the interpretation tentatively put forward in Ref. 3 that the 3.45 eV line is made of two different lines linked to an A-exciton transition for the lowest energy line and a B-exciton transition for the high energy line.

Note that as our polarization experiment is performed in an anisotropic medium, it is not possible to directly deduce the dipole orientation from PL polarization measurements. For isolated GaN NWs, it has been shown that the NW geometry favors coupling to the electromagnetic modes polarized along the NW axis. In other words, an isotropic dipole would radiate light mainly polarized along the NW axis. Our geometry is quite different from an isolated NW as we are dealing with an ensemble of dense nanowires that acts as an effective medium with a large birefringence. While it is beyond the scope of this article to analyze the spontaneous emission anisotropy in our specific geometry, it can safely be said that the 3.45 eV transition is not polarized like an A-exciton and has a sizeable fraction of its dipole along the c-axis.

This polarization resolved measurement has important consequences. As the D0X(A) and the 3.45 eV line do not have the same dipole orientation, they have different far-field diagrams so that the intensity ratio of these two lines depends strongly on the collection geometry, i.e., the collection angle with respect to the c-axis (most PL experiments...
are done in the same configuration with a collection axis aligned with the c-axis) and the collecting numerical aperture. This last parameter is often not given in publications on the topic and it is thus difficult to compare PL experiments on GaN NWs stemming from different publications, in which the PL collection geometries might vary. More importantly, while the far-field emission diagram from a given dipole in a bulk material can be easily modeled, the situation is quite different for a nanowire ensemble which is a highly anisotropic light-scattering medium. While there is no literature dealing with the far-field emission in a dense nanowire ensemble as a function of dipole orientation, Maslov and co-workers have calculated the far-field emission from the fundamental guided mode of an isolated nanowire.\(^{28}\) It turns out that the emission pattern is angularly quite broad and that there even is some backscattering at the nanowire tip. Moreover, the spontaneous emission rates can vary considerably for an emitter inside an isolated nanowire depending on its dipole and its radial position inside the nanowire.\(^{29}\) It is thus not possible to draw any conclusion from the mere measurement of the intensity ratio of the D0X(A) and the 3.45 eV lines unless a proper modelization of the electromagnetic modes as a function of NWs densities and diameters is done. It has notably been reported that the intensity of the 3.45 eV line is stronger relatively to the D0X line in low density samples.\(^{3,10,11}\) It might well be that for low density samples, the emission stemming from the 3.45 eV line is better collected in a standard PL experiment than in dense samples. These considerations on the far-field of the PL stemming from NWs show that these effects should be taken into account when comparing relative intensities of the 3.45 eV line and the D0X(A) line. They could indeed explain the variations that seem to appear from one study to another.

In order to further investigate this 3.45 eV transition, we performed magneto-photoluminescence experiments so as to measure the diamagnetic shift and the Zeeman splitting of these transitions and compare them with the literature on magneto-photoluminescence of GaN. Indeed, while the polarization properties of optical transitions are eventually a convolution of purely electronic properties (the dipole orientation of the transition) and electromagnetic properties (the intensity and orientation of the electromagnetic modes at the emitter’s location), the magnetoPL properties can be directly linked to the electronic symmetries of the exciton wavefunction. Figure 3 shows the magnetic field evolution of the PL in Voigt configuration (magnetic field perpendicular to the light wavevector, i.e., perpendicular to the NWs axis) at 4 K. One sees clearly that the donor bound exciton line splits in magnetic field. The splitting at 22 T that we measure is 2.2 meV, yielding a g-factor of 1.75 while the diamagnetic shift coefficient we measure on the D0X(A) transition in 2.2 meV, yielding a g-factor of 1.75 while the diamagnetic magnetic field. The splitting at 22 T that we measure is One sees clearly that the donor bound exciton line splits in light wavector, i.e., perpendicular to the NWs axis) at 4 K. In order to further investigate this 3.45 eV transition, we performed magneto-photoluminescence experiments so as to measure the diamagnetic shift and the Zeeman splitting of these transitions and compare them with the literature on magneto-photoluminescence of GaN. Indeed, while the polarization properties of optical transitions are eventually a convolution of purely electronic properties (the dipole orientation of the transition) and electromagnetic properties (the intensity and orientation of the electromagnetic modes at the emitter’s location), the magnetoPL properties can be directly linked to the electronic symmetries of the exciton wavefunction. Figure 3 shows the magnetic field evolution of the PL in Voigt configuration (magnetic field perpendicular to the light wavevector, i.e., perpendicular to the NWs axis) at 4 K. One sees clearly that the donor bound exciton line splits in magnetic field. The splitting at 22 T that we measure is 2.2 meV, yielding a g-factor of 1.75 while the diamagnetic shift coefficient we measure on the D0X(A) transition in NWs is \(\Delta D_{1}^{\text{D}} = 6.5 \times 10^{-7}\) eV T\(^{-2}\). We conclude, as expected, that the nanowire geometry and the confinement have a negligible influence on the magnetic properties of excitons as these numbers are very close to what was measured in homoepitaxial GaN layers (\(g_{\text{D}}^{\text{D}} = 1.87, D_{1}^{\text{D}} = 7.3 \times 10^{-7}\) eV T\(^{-2}\)).\(^{30}\) On the opposite, the 3.45 eV line does not seem to shift nor split. We however note that the linewidth of the 3.45 eV line is around 5 meV, so that small splittings might not be visible. The TES magnetoluminescence properties were analyzed in detail in Ref. 31. A wealth of peaks appears at high magnetic field, corresponding to various final states of the TES transition. In Fig. 6 of Ref. 31, a splitting of 6 meV is measured at 22 T between the extreme lines (A2 and A4). We show in Fig. 4 our data at 0 T and 22 T together with a curve obtained from our 0 T data split by 6 meV. It appears clearly that if the 3.45 eV line in NWs were a TES, a clear magnetoluminescence distortion of our spectra would be observed. This is further confirmed by magnetoluminescence experiments performed in polarized Faraday configuration (magnetic field along the NW axis). In that case as seen in Fig. 5, the D0X(A) line barely splits. Indeed, in this configuration, the effective g-factor is reduced compared to the Voigt configuration and is 0.64 (Ref. 30) so that the Zeeman splitting is 0.8 meV at 22 T, i.e., smaller than the transition linewidth. The polarization resolved spectra\(^{32}\) allow us to extract a g-factor on our sample of 0.88, close to the measured value on
bulk GaN of 0.64. The TES line in bulk GaN is however splitting and shifting as well in Faraday configuration as indicated in Fig. 5 of Ref. 31. If one takes only into account the main line at high magnetic field, i.e., the A2 line, a red-shift of 3 meV is measured at 22 T. This again would clearly be seen in our sample if it were a TES as shown in Fig. 6. These magnetoluminescence experiments thus confirm that the 3.45 eV line in NWs cannot be attributed to a TES.

IV. FURTHER EXPERIMENTS, CONCLUSION, AND PROSPECTS

We have performed further experiments to gain more insight on the 3.45 eV line. While this line is observed in all the GaN NW samples we grow by PA-MBE, we note that when a slight magnesium doping is introduced, it disappears (Fig. 7). This phenomenon was also observed in Ref. 10, in which the authors argue that this is in favor of the attribution of the 3.45 eV line to Gallium vacancy defects (VGa) on the nanowire sidewalls, as these defects appear more easily in n-type samples. While this last argument might not be very convincing in the case of nanowires in which surface Fermi level pinning probably dominates regardless of the incorporated species, the adjunction of Mg during growth might play a role in the formation of the nanowires. It is indeed known that for PA-MBE growth of Ga-polar GaN, Mg acts as a surfactant during the growth. This was also seen on the (11–22) semipolar orientation, but was not studied for m-plane growth. It can still tentatively be inferred that Mg acts as a surfactant during growth on the m-plane side facets of the nanowires, thus, preventing the formation of a particular surface defect which could be responsible for the 3.45 eV emission line. It is by the way interesting to see that in our Mg-doped nanowires, the A0X(A) linewidth is 800 eV while the D0X linewidth is 680 eV: these linewidths are much smaller than those reported for PA-MBE grown GaN nanowires so far. In this respect, we note that Ref. 9 argues that “the random distribution of donor sites could be an intrinsic origin of the broadening of all PL lines involving donors,” while Ref. 12 argues that “the minimum reported linewidth of 2–3 meV for NW ensembles is intrinsic and not caused by residual strain but rather by the energy difference between excitons bound to bulk and surface defects of 3–4 meV.” Clearly our experimental results seem to be in contradiction with such assertions as much smaller linewidths are measured in our case. A review of the literature shows that linewidths of 1.2 meV were reported on ensembles of MBE grown nanowires, however, in the case of large diameters (90–150 nm) which is thus not contradictory with the explanation of a broadening induced by a distribution of donors more or less close to the nanowire surface. Linewidths of 1.5 and 1.6 meV were reported for nanowires with smaller average diameters. In the case of our nominally undoped samples (D0X linewidth 1.2 meV) and Mg-doped sample, the diameters are in the 30–50 nm range. The
fact that the linewidth of the D0X is a factor of 2 lower in the Mg-doped sample compared to the state-of-the-art of nominally undoped samples does not necessarily contradict the articles proposing that the linewidth is limited by the distribution of the donors inside the nanowires. It may well be that due to the Mg surfactant effect the distribution of donors (or of optically active donor giving rise to a D0X(A) transition) is modified compared to an undoped sample, with for instance fewer active donors close to the surface. This remains still quite speculative and would require studies to determine the radial distribution of dopants in such nanowires to be validated.

The next set of experiments deals with the spectroscopy of single nominally undoped nanowires by microphotoluminescence. The first experiment studies nanowires removed from their growth substrate and consequently dispersed on a SiO$_2$ on Si substrate with low enough density to study single NWs. The low temperature PL of three different nanowires is shown in Fig. 8. It appears that some nanowires exhibit luminescence at both D0X(A) transition and 3.45 eV transition, while others show luminescence only at either of these lines. As interactions with the host substrate may alter the physical properties of the dispersed nanowires, we also did similar experiments on a low density sample to study nanowires standing on the growth substrate, similarly to what was done in Ref. 13. In that case, comparable results are obtained as depicted in Fig. 9 with the presence of either of these lines or of both of them depending on the nanowire that is studied. These results are compatible with previous results published on single GaN NW PL.12,13

We can now sum-up the current knowledge on the 3.45 eV line in PA-MBE grown nanowires. (i) Its dipole has a sizeable component along the c-axis. (ii) It does not split nor shift as a function of magnetic field as a TES should. (iii) It disappears in case of Mg doping. (iv) The microPL of single nanowires- either grown as dense nanowires and subsequently dispersed or grown at high temperature to form low density samples- shows that some nanowires exhibit either the 3.45 eV line or the D0X line, or both of them. (v) Some samples do not show the 3.45 eV, particularly those with large (>100 nm) diameters.

To conclude this study, while there is at this stage no certainty as to the exact attribution of the 3.45 eV transition, our experiments allow to refute the TES interpretation. Several articles have attributed the 3.45 eV transition to a surface-related transition: this is a natural explanation concerning nanowires which have a large surface to volume ratio, and is supported by some experimental facts, notably the spectral evolution with time reported in Ref. 39. We believe that this interpretation of a surface defect is further confirmed by our polarization-resolved experiment. Indeed, if such a shallow transition compared to the band-edge was due to an exciton bound to some defect of the crystal, it would be expected to follow the polarization selection-rules of an A-exciton in low temperature PL. This however does not hold for an exciton bound to a surface defect for which the wavefunctions are not built on the standard Bloch functions of the bulk crystal. The hypothesis notably discussed in Ref. 10 of an exciton bound to a surface Ga vacancy due to the N-rich growth conditions remains compatible with all experimental results reported so far; this compatibility being however mainly due to the ignorance on the optical properties of such a transition. Our work however shows that some nanowires do not show the 3.45 eV line, meaning that the particular defect responsible for the 3.45 eV line is absent in some nanowires. In other words its distribution among the nanowires has a low average number, at most of a few units (we did not measure enough nanowires to have more precision on this distribution, the case of nanowires that do not show the 3.45 eV line is however not rare). Now it has to be noted that for a typical PA-MBE grown GaN nanowire (diameter 30 nm, length 1 μm), there are about $5 \times 10^5$ atoms on the surface. It thus seems unlikely that under N rich conditions only a few vacancies on average per nanowire are formed, and none in some nanowires. It is thus at this stage still difficult to conclude on the attribution of this particular line.
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