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Incorporation of Europium into GaN Nanowires by Ion Implantation

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ABSTRACT

Rare earth (RE) doped GaN nanowires (NWs), combining the well-defined and controllable optical emission lines of trivalent RE ions with the high crystalline quality, versatility and small dimension of the NW host, are promising building blocks for future nanoscale devices in optoelectronics and quantum technologies. Europium doping of GaN NWs was performed by ion implantation and structural and optical properties were assessed in comparison to thin film reference samples. Despite some surface degradation for high implantation fluences, the NW core remains of high crystalline quality with lower concentrations of extended defects than observed in ion implanted thin films. Strain introduced by implantation defects is efficiently relaxed in NWs and the measured deformation stays much below that in thin films implanted in the same conditions. Optical activation is achieved for all samples after annealing and, while optical centres are similar in all samples, Eu^{3+} emission from NW samples is shown to be less affected by residual implantation damage than for the case of thin films. The incorporation of Eu in GaN NWs was further investigated by nano-cathodoluminescence and X-ray absorption spectroscopy (XAS). Maps of the Eu-emission intensity within a single NW agree well with the Eu-distribution predicted by Monte Carlo simulations suggesting that no pronounced Eu-diffusion takes place. XAS shows that 70-80% of Eu is found in the 3+ charge state while 20-30% is 2+ attributed to residual implantation defects. A similar local environment was found for Eu in NWs and thin films: for low fluences, Eu is mainly incorporated on substitutional Ga-sites while for high fluences XAS points at the formation of a local EuN-like next neighbour structure. Results reveal the high potential of ion implantation as a processing tool at the nano-scale.

INTRODUCTION

Rare earth doped GaN thin films have been the subject of intense research in the past two decades due to their promising properties for optoelectronic and spintronic applications[1]. In particular, doping with europium led to the demonstration of the first low voltage GaN:Eu light emitting diode (LED)[2]. The typical red luminescence of the Eu^{3+} ions is of particular interest since the efficiency of conventional III-nitride LEDs drops significantly in the green and red spectral region[3]. While GaN:Eu films have been fabricated by various techniques such as in-situ doping during molecular beam epitaxy (MBE)[4] and metal organic vapor phase epitaxy (MOVPE)[2] or ex-situ doping by ion implantation[5,6], studies on Eu-doped GaN nanowires (NWs) are still scarce[7,8,9]. Given the demonstrated advantages of GaN NWs (for example grown by MBE) over epitaxial films, including low dislocation densities, their ability of efficient strain relaxation even on lattice mismatched substrates and improved light extraction[10], functionalization of these NWs with optically active ions could lead the way to new applications and device designs. However, in-situ doping of nanowires is challenging due to frequently occurring segregation of second phases or morphology changes. Furthermore, so called self-purification processes cause the expulsion of dopants from the bulk of the NWs to their surface. Aravindh and Roqan, based on density functional theory (DFT) calculations, suggest that the most likely incorporation sites of the rare earth Gd in GaN NWs are at the surface[11]. Xu et al.[7] fabricated Eu-doped GaN nano-needles via a vapor transport route with the dominant Eu^{3+} emission line, corresponding to the $^5D_0 \rightarrow {}^7F_2$ intra-atomic transition, at 611 nm. Typical wavelengths for the main line of various optically active Eu^{3+} centers in GaN:Eu films lie in the range from 618 to 625 nm[12]. The large shift of the emission to higher energy for the case of the nano-needles can be attributed to surface effects[7]. Confinement effects should play a negligible role in this behavior since only

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minor shifts due to site multiplicities or different strain states were reported for rare earths incorporated in quantum dots and NWs [13,14]. Sekiguchi et al.[9], reported the Eu-doping of GaN NWs during MBE growth leading to similar optical centers as in thin films while exhibiting strongly reduced concentration quenching. Despite these highly promising results, doping led to morphology changes and even polycrystalline growth for high Eu concentrations[9]. Ion implantation was suggested as a promising alternative to introduce dopants in NWs without affecting their morphology[15,16]. Indeed, establishing the ion implantation technique as processing tool at the nanoscale could facilitate the use of doped NWs as building blocks for future nanodevices in electronics and photonics. Rodrigues et al.[8] studied Eu implantation in GaN NWs using fluences of $5x10^{13}$ and $3x10^{15}$ at/cm^2 and incidence angles with respect to the c- axes of the vertically aligned NWs of 20 and 30°. It was shown that annealing leads to effective optical activation of the Eu^{3+} emission with higher intensity and reduced temperature quenching compared to GaN films prepared in the same conditions. Furthermore, the dominant optical center is the same in NWs and films and no significant changes were seen in the spectral shape for different fluences and implantation geometries[8].

Nevertheless, ion implantation is inherently connected with defects created by the bombardment with heavy and energetic ions which can deteriorate structural and optical properties. Implantation damage build-up processes in GaN thin films are relatively well understood. In particular, they are dominated by strong dynamic annealing which leads to the efficient recombination of point defects already during the implantation but also promotes the formation of thermally stable extended defects such as point defect clusters and stacking faults[17,18,19,20]. Only few studies address implantation damage mechanisms in GaN NWs[21,22,23,24]. Molecular dynamics simulations

for Er implanted GaN NWs reveal high sputtering yields and an accumulation of defects close to the surface[24]. High sputtering yields and surface defects are furthermore consistent with the experimental observation of blisters at the surface of GaN NWs after implantation[22]. Both simulations[24] and experiments[23] reveal the introduction of hydrostatic strain by the implantation defects. In contrast, other experimental studies suggest increased dynamic annealing in GaN NWs as compared to bulk material[21] and for the special case of Pr implanted GaN NWs, Pr related luminescence was even enhanced by the interaction with certain defects created by the implantation and annealing processes[23]. Thermal annealing of implantation damage is challenging in GaN due to the thermal dissociation of the crystal starting at approximately 800 °C[25]. This issue is aggravated for the case of NWs due to the increased surface area to volume ratio. The application of special capping layers or annealing under high nitrogen pressure, successful in GaN layers[26,27], are not practical for NWs. Nevertheless, it was shown that rapid thermal annealing at 1000 °C can effectively reduce implantation damage and optically activate rare earth ions[8,23].

In this work we report a comprehensive study of the structural alterations, in particular strain and morphology changes, induced by implantation of GaN NWs. Furthermore, we advance a microscopic model for the incorporation of implanted Eu in GaN NWs and thin films.

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METHODS

Vertically aligned GaN NWs have been grown by molecular beam epitaxy on (111) Si substrates using a thin (2-3 nm) AlN buffer layer. The NW growth was performed for ~13 hours at 800 °C in nitrogen rich conditions; details were published previously[28]. Active N flux was provided by a radio frequency N_2 plasma cell and Ga flux by a standard effusion cell. N-rich conditions were used, i.e. a Ga/active N flux ratio of about 1/3. Deoxidation of the (111) Si substrate was performed by dipping in a 15%-HF: deionized water bath, followed by a smooth annealing in vacuum at 300 °C and next at 900 °C till reflection high energy electron diffraction (RHEED) observation of a clear 7×7 reconstruction, indicative of a clean surface[28].

Figs. 1a-d show scanning electron microscopy (SEM) images of the as-grown GaN NWs for sample set 1 revealing an average diameter of ~50 nm close to the center of the wafer (Fig. 1a and b) and ~100 nm towards the periphery (Fig. 1c and d) leading to increasing coalescence when approaching the edge of the wafer. The NW length varied between 2000 and 2500 nm and the NW density ranged from 2 to 7×10^9 cm^{-2} increasing towards the wafer edge. In the zones of low NW density close to the center, a 2D layer, consisting of coalesced GaN pyramids[28], is visible at the base of the NWs (Fig. 1a).

A second set of samples, specially designed for the synchrotron measurements, showed a more homogeneous NW density of 9×10^9 cm^{-2} across the wafer and no 2D layer (Figs. 1e and f).

Samples were implanted at room temperature with 300 keV Eu ions to fluences ranging from 1×10^{13} at/cm^2 to 5×10^{15} at/cm^2. Some preliminary results for implantation at 600 °C are also discussed. The implantation was done in six steps rotating the sample sixty by sixty degrees in the azimuthal angle while the incidence angle between the beam and the NW axes was 20° for sample set 1 and 40° for sample set 2. This procedure yields a distribution of Eu and implantation defects which is close to rotationally symmetric around the central axis of the NWs and prevents the NWs from bending due to strain

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gradients. The final Eu distribution inside the NWs is complex and depends on the implantation angle, NW diameter and NW density. The three dimensional distribution of Eu and defects has been studied using Monte Carlo simulations implemented in the TRI3DYN code[29],[30],[31]. This code is based on the binary collision approximation and allows simulating dynamic effects of ion irradiation in three dimensional structures.

Annealing of the samples was performed for holding times of 30 s at 1000 °C with a heating ramp of 30 °C per second in an ANNEALSYS halogen lamp rapid thermal processor under flowing nitrogen.

In all cases, thick (~3 μm) GaN layers (purchased from Lumilog) grown by metal organic chemical vapor deposition on (0001) sapphire were implanted and annealed simultaneously for comparison. Additionally, a reference layer for extended X-ray absorption spectroscopy (EXAFS) measurements was implanted along the c-axis to a low fluence of $1x10^{14}$ at/cm^2 and annealed in optimized high temperature high pressure (HTHP) conditions of 1400 °C and nitrogen pressure of 1 GPa[32].

X-ray diffraction (XRD) was performed on a high resolution Bruker D8 Discover diffractometer using a Göbel mirror to yield a parallel beam and an asymmetric 2-bounce Ge (220) monochromator to choose the $CuK_{\alpha1}$ line. 2θ–θ curves were acquired with a 0.2 mm slit placed before the monochromator and a 0.1 mm slit in front of the scintillation detector.

Conventional transmission electron microscopy (TEM) and high resolution scanning-TEM (STEM) were carried out on selected samples. The NWs were dispersed on the TEM grid without any further sample preparation. Conventional TEM investigations were performed with a JEOL 2100 microscope and atomically resolved STEM high angle annular dark field images (HAADF) have been acquired in a Nion UltraSTEM 200 both operated at 200 keV.

Cathodoluminescence (CL) spectroscopy was carried out at room temperature using a Hitachi S2500 SEM and a Hamamatsu PMA-11 charge coupling device camera. The acceleration voltage was V_{acc} = 5 kV yielding an electron penetration depth in GaN of ~70 nm as estimated by the Monte Carlo code CASINO[33]. The beam was defocused to several hundreds of micrometers diameter in order to limit the excitation density and

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3 mitigate the strong intensity quenching of the Eu^{3+} lines observed for a focused beam. The electron beam hits both the top surface and parts of the side facets of the NWs with an incidence angle of 25° towards the surface normal. Selected NW samples were furthermore analyzed using nano-CL on single NWs in a STEM (VG HB501) operated with 80 keV electrons (typical electron current 60 pA) with the sample kept at 150 K[34].

X-ray Absorption Spectroscopy (XAS) measurements were conducted on both FAME (BM30B) and SPLINE (BM25) beamlines at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The main optical element of both beamlines is a two-crystal monochromator (Si (220) for FAME and Si (111) for SPLINE) with a cooled first crystal and a sagitally bent second crystal[35,36,37]. Two bendable Rh-coated mirrors located before and after the monochromator ensure harmonics rejection. XAS spectra were recorded at the L_{III} edge of Eu (6977 eV) in fluorescence mode with a multi-element energy-resolved Ge detector. Experiments were conducted at room temperature except for the very low fluence GaN film reference sample which was measured at 100 K to benefit from an increased signal-to-noise ratio that compensates for the very low amount of implanted Eu. The energy calibration was made using a Fe reference foil (7112 eV). Measurements were performed in grazing incidence geometry (with an angle of ~5-15° between the beam and the sample surface) in order to maximize the signal from the implanted layer. Base line extraction of XAS spectra as well as EXAFS analysis were conducted using the well-known DEMETER comprehensive system for processing and analyzing XAS data (that includes *ATHENA, ARTEMIS and IFEFFIT programs*)[38]. For meaningful quantification, we took into account the polarization of the X-ray beam. Further details on XAS measurements and data analysis are given in the supplementary materials.

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RESULTS AND DISCUSSION

1. Dynamic Monte Carlo simulations

TRI3DYN simulations have been performed for three relevant configurations: implantation of Eu at 20° tilt into NW arrays with either i) 50 nm diameter and an areal density of 2×10^9 cm^{-2} or ii) 100 nm diameter and an areal density of 7×10^9 cm^{-2} (corresponding to sample set 1 with samples from the center or the edge of the wafer, respectively) and iii) implantation at 40° tilt into NW arrays with 100 nm diameter and an areal density of 9×10^9 cm^{-2} (corresponding to sample set 2 used for XAS measurements). A regular two-dimensional square configuration of the nanowires with the desired areal density is modelled by the choice of periodic lateral boundary conditions. For rotational symmetry around the axis of the nanowires, the structure is randomly rotated at each ion incidence. An extended description of the simulation, including the choice of critical parameters, is included in the Supplementary Information. Besides the ion energy and NW diameter, the implantation geometry and NW density will determine the distribution of Eu in the NWs due to shadowing effects by neighboring NWs. All results are shown for a final fluence of 3×10^{15} at/cm^2. Fig. 2 shows the simulated elemental distributions (Ga, N, Eu) in a longitudinal slice of 8 nm thickness along the NW length for cases i) and ii). Note that for case ii) in the simulation a NW length of 1000 nm was assumed allowing a better lateral resolution and saving computational costs. Fig. 2 also gives the distribution of implantation damage given in displacements per atoms (dpa). For case i) (low density of 50 nm diameter NWs), implantation yields an almost homogeneous distribution of Eu along the entire length of the wire. A slightly higher Eu concentration is found at a depth of ~55 nm corresponding to ions that enter the NW from the top surface. This is seen better in Fig. 3 showing the average Eu-concentration along the NW length for the three cases. Accordingly, the implantation damage for case i) is also distributed homogeneously along the entire NW with some increased displacements close to the upper surface due to ions entering the NW from the top. According to the simulations, for this low density of NWs only about 54% of all ions are stopped within the NWs while the remaining 46% are implanted into the Si-substrate. Indeed, RBS spectra on the template after removing

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the NWs by scratching and ultrasound cleaning showed that a large fraction of Eu was implanted into the substrate and 2D layer in samples with low NW density. For case ii) (high density of 100 nm diameter NWs - see bottom row of Fig. 2), the distribution of Eu and implantation damage is less homogeneous. A large fraction of ions enters the NWs through the top surface leading to an increased Eu concentration in the first ~100 nm of the NW (Fig. 3) as well as to increased lattice damage close to the NW tip similar to implantation in planar substrates. For these implantation conditions simulations show that 98.6% of all ions are stopped within the first 1000 nm of the NW (see Fig. 3). Most ions entering through the lateral surface will not reach the NW center due to the higher NW diameter for case ii) and Eu as well as defects will accumulate close to the rim of the NWs. The lateral distribution of Eu is shown in Fig. 4 where the top row shows an integration over the first 50-150 nm of the NW tip where the Eu distribution is influenced by ions entering via the top surface leading to an almost homogeneous distribution of Eu. For integration over the remaining NW base (bottom row of Fig. 4) the Eu distribution is determined by ions entering the NW from the side facets. For the 50 nm diameter NWs this leads to a maximum Eu concentration close to the central axis of the NW while for the 100 nm diameter NWs the doping concentration is higher close to the side facets and decreases towards the central axis.

For optical measurements and XRD, Eu reaching the silicon substrate does not interfere with the signal from the NWs (note that Eu is optically inactive in Si). However, for XAS measurements it is important to avoid any Eu reaching the substrate since all Eu ions will contribute to the measured signal. Therefore, the second set of samples was implanted using an incident angle of 40°. This geometry, together with the high and homogeneous density of NWs and the absence of a 2D layer, assured that Eu was only implanted into the GaN NWs and not into the Si-substrate or the coalesced GaN 2D layer at the base of the NWs. Fig. 3 clearly shows that the Eu distribution is concentrated in the top 500 nm of the NWs. In fact, the simulations indicate that 99.3% of all ions come to rest inside the NWs while the remaining 0.7% are being backscattered.

An additional feature observed in the elemental maps in Fig. 2 is a preferential loss of nitrogen due to sputtering, leading to a slight N-deficiency in the bulk of the NW, in particular, in the regions of higher damage concentration. This is in agreement with

Molecular Dynamics simulations of ion implantation in GaN NWs[39]. A slight enrichment in N is observed at the outer surface, which is attributed to the redeposition of preferentially sputtered N atoms from the surrounding nanowires.

2. Strain and morphology

Fig. 5 shows XRD (0004) 2θ–θ curves for the first set of NWs and films implanted to different fluences of 300 keV Eu ions at 20° incidence. For the thin film reference samples, the implantation leads to the formation of a satellite peak at lower 2θ angle than the main Bragg peak clearly visible for the lowest fluence. The hydrostatic strain caused by implantation defects leads to an expansion of the c-lattice parameter within the implanted volume as it was first reported by Liu et al. for c-plane GaN layers[40]. With increasing fluence the induced strain increases and the satellite peak shifts to lower angles. For fluences starting from 5×10^{14} at/cm^2, the diffraction intensity of the satellite peak decreases strongly and XRD becomes insensitive to further defect formation. Similar curves have been reported for Eu implantation along the c-axis of GaN except that the saturation regime, when the diffraction pattern does not evolve further, is only reached at higher fluences (1×10^{15} at/cm^2)[41]. This saturation was attributed to the formation of a dense network of extended defects leading to plastic deformation and strain relaxation. Many authors have reported similar strain formation in GaN for different implantation conditions[42,43,44]. In fact, it was suggested that strain induced by implantation defects is the driving force behind the defect mobility and dynamic annealing in GaN leading to the change of defect microstructure as the fluence increases[45]. Detailed XRD studies on GaN NWs and NW heterostructures showed that, due to their vertical alignment, NWs can be studied by laboratory XRD in a similar way as planar heterostructures[46,47]. However, the diffraction intensity is strongly reduced

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3 due to the reduced sample volume and the fact that, due to the relatively high tilt between NWs, only a fraction of them will be well-oriented to satisfy the Bragg condition and contribute to the Bragg peak intensity. Moreover, the line shape and broadening are influenced by the inclination of the NWs normal to the scattering plane and inhomogeneous fluctuating strain[47]. Indeed, the XRD patterns of the as-grown NWs (see Fig. 5a) show the typical non-Gaussian peak broadening which Kaganer et al. attributed to random distortions caused by lattice defects at the interface between the NWs and the substrate and at joints between coalesced NWs[47]. Nevertheless, similar to the layers, a second peak formed after implantation is clearly visible, which is strongly overlapped to the Bragg peak arising from unimplanted GaN. Two main differences can be pointed out when comparing these diffraction patterns to those of the thin film reference samples. First, the satellite peaks in NWs have a comparable intensity as the peak corresponding to unimplanted volume. This can be understood by the fact that the ratio of implanted/unimplanted volume in the NWs is much larger since not only a thin surface layer is doped but ions can enter through the side facets of the wires and penetrate the entire wire width. Like this, only the bases of the NWs remain unimplanted due to shadowing by the surrounding NWs. It is worth mentioning that we did not see any significant difference in the XRD patterns from the wafer center or the peripheries suggesting that the 2D layer present in sample set 1 has a similar behavior as the NWs. Second and more importantly, the maximum strain that is reached is much lower in the NWs than in the thin films (see upper x-axis in Fig. 5 where the angle was converted to perpendicular strain as $\varepsilon^{\perp} = (c_{exp} - c_0)/c_0$, with c_0 the c-lattice parameter of the as-grown GaN and c_{exp} the expanded c-lattice parameter as determined from the 2θ position of the XRD curves). While in thin films already for the

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lowest fluence the incorporated perpendicular strain exceeds 0.5%, this value is never reached in the NWs even for the highest investigated fluence. The lower strain state in NWs can be attributed to more efficient relaxation mechanisms in low dimensional structures especially since implantation defects in NWs are expected to accumulate at the surface. The higher vacancy concentration (relative to interstitial defects) suggested by molecular dynamics simulations may also play a role[24]. Furthermore, it is possible that a biaxial component of defect induced strain increases the perpendicular strain in bulk material due to the in-plane stress imposed by the unimplanted bulk[48] while in NWs the *a*-lattice parameter is freer to expand. Strain in the *c*-plane is indeed predicted to occur by molecular dynamics simulations although with lower magnitude than the perpendicular strain[24]. Unfortunately, it was not possible to measure the *a*-lattice constant in the present work due to the small material volume in NW samples and the low intensity of the asymmetric XRD reflections. Synchrotron diffraction measurements should be done to clarify this point.

The effect of annealing on XRD $2\theta-\theta$ curves is shown in Fig. 6 for the NW samples implanted with 40° tilt and annealed at 1000 °C. In agreement with the Monte Carlo simulations showing that only the upper part of the NWs is implanted in this geometry, the intensity ratio of the diffraction peaks corresponding to implanted and virgin material is lower than for sample set 1. After annealing the curves become symmetric and resemble those of the as-grown samples suggesting that the defect induced strain is efficiently removed even for the highest fluence of 5×10^{15} at/cm^2. Although direct comparison of the curves should be done with caution due to lateral inhomogeneities of the samples, a slight broadening of the curves for the annealed NWs implanted to the

highest fluences is probably due to remaining implantation defects and surface degradation.

For thin film samples efficient strain recovery is only seen for the lowest fluence of 1×10^{13} at/cm^2; for higher fluences it is not even achieved after annealing at 1450 °C as reported previously and diffraction curves remain asymmetric after annealing[32,49].

There is no significant difference between the XRD results on samples implanted with 20° and 40° tilt. We recently showed that the defect structures in thin films strongly depend on the surface orientation (a-plane, c-plane or m-plane)[50], however, the influence of the exact implantation geometry and its impact on damage in NWs needs further investigations.

The morphology changes upon implantation were investigated by TEM for the different fluences. Up to a fluence of 5×10^{14} at/cm^2 no significant change has been noticed in the NW morphology (Fig. 7a). All the nanowires exhibit well defined clean facets and no amorphization. Their diameter progressively decreases towards the top which is probably due to the growth process. At this fluence, the nanowire may exhibit one or two basal stacking faults[51] across the entire width (marked with white arrows in Fig. 7b). Such defects are probably generated by the ion implantation; indeed they are known to constitute the basic deformation channel for GaN thin films during such an implantation process[19]. By the fluence of 1×10^{15} at/cm^2, two types of structural changes are seen to take place in the nanowires. As can be seen in Fig. 7c, nanowires can bend at the level of the tip (T), but also at their base (B), and this can be accompanied by rounding at the tips. However, at this fluence, most of the observed nanowires stay upright as shown by the weak beam image recorded with g = 0002 (Fig. 7d). The exhibited contrast indicates

that, although the nanowire has been damaged, the core retains a crystalline structure, all along the nanowire. This is also visible through the lattice fringes which disappear towards the outer part of the wire which then displays a random contrast indicating that this area has undergone amorphization. This is in contrast with our earlier reports on bulk GaN where up to the highest fluences the material was shown to transform to nanocrystalline form instead of becoming amorphous under ion implantation[52]. For this fluence and beyond, the formation of surface defects such as blisters (Fig. 7e) is consistent with the high sputtering yields suggested by molecular dynamics simulations[24] and previous experimental results[22]. For the highest fluence (3×10^{15} at/cm^2), only a limited number of NWs retain their integrity when transferred to the TEM grid for observation (Fig. 7f); in this case the rounding of the tips is more prominent and more stacking faults can be seen in the less damaged parts of the NWs (Fig. 7g). Nevertheless, compared to GaN epitaxial layers, the density of stacking faults is very small, which means that the formation of such defects is not the dominant mechanism in these low dimensional structures. At this fluence, most of the nanowires become brittle leading to the easy breaking-off of the top which is the most sollicitated part of the NWs when they are transferred to the TEM grid (Fig. 7h).

After annealing at 1000 °C, scanning TEM (STEM) high angle annular dark field (HAADF) was carried out as shown in Fig. 8 for a NW implanted with 1×10^{15} at/cm^2. As can be seen in Fig. 8a, the nanowire surface is no longer limited by large and regular crystallographic faces. In this low magnification micrograph, the roughness is clearly visible on the sides and influences the contrast of the whole image as indicated by the darker spots which reveal that the corresponding thickness is smaller than that of the surrounding areas. Most interesting, as shown in figure 8b, the amorphous parts as well

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as the surface blisters have completely disappeared, which means that the amorphous areas may have recrystallized during the annealing process or evaporated. All along the annealed nanowire, no basal stacking faults can be seen anymore, which is an indication that they have been removed. Only in very few areas, however, some local irregular features have been noticed (Figs. 8c and d) which may correspond to small extended defects possibly consisting of three extra planes. This behavior is still under investigation.

3. Optical activation

Despite the pronounced surface degradation but consistent with the high crystalline quality of the NW core, where most of the Eu ions should come to rest, all samples show optical activation of the Eu^{3+} ions with the dominant line, corresponding to the $^5D_0\rightarrow{}^7F_2$ transition, at ~622 nm. The inset in Fig. 9b presents the CL spectra of a NW and a thin film sample both implanted to a fluence of 1×10^{14} at/cm^2. The spectra are representative for all fluences and confirm that the Eu^{3+} optically active centers are similar in NWs and thin films. This is in agreement with the detailed photoluminescence spectroscopy study performed on a sub-set of the samples studied here and which showed that the dominant Eu^{3+} center is the same in NWs and films despite a small shift in the line positions presumably due to different strain states of the GaN hosts[8]. These observations were independent of implantation fluence and geometry. In the following we focus on the emission intensity. The CL intensity of the main Eu^{3+} emission line at 622 nm is plotted in Fig. 9 for NWs (a) and thin films (b) as a function of the fluence. The values were achieved by measuring three spectra in different points of the sample, which varied only slightly, and averaging the measured intensities. For the NW sample this was done in two regions with high and low NW density. For the case of the doped

thin films (Fig. 9b) the intensity first increases with the fluence up to 5×10^{14} at/cm^2 and then decreases again due to the severe lattice damage which could not be removed by thermal annealing. This behavior is similar to that observed previously for implantations performed along the c-axis. However, in the latter case the decrease of intensity only occurs at higher fluences[53] which can be attributed to the lower damage level when implantation is performed in channelling geometry (which promotes the steering of ions along the atomic rows and reduces the direct collisions with the target nuclei)[42,54]. For the case of the NWs, distinct behaviours are observed for regions with high or low NW density. For low NW density a saturation of the emission for high fluences is observed. Although no pronounced intensity decrease occurs as for the thin films, the similar behaviour might suggest that a large fraction of Eu was implanted into the 2D layer at the base of the NWs and with a similar behaviour as that observed for thin films. For high NW density, on the other hand, no saturation or quenching is observed up to the highest measured fluence. However, the increase of emission intensity is much lower than expected when assuming a direct proportionality between Eu concentration and emission intensity. This implies that most of the implanted Eu ions in high fluence samples are not optically active. This can be either due to a less effective energy transfer from the GaN host to the Eu^{3+} ions, the quenching of luminescence due to the formation of defects acting as non-radiative recombination centres or due to the incorporation of Eu in inadequate lattice sites, for example sites which do not support the 3+ valence state of the Eu ions.

In order to get a more microscopic view of Eu incorporation in NWs, nano-CL was performed on single NWs as presented in Fig. 10. Fig. 10a shows the CL spectra acquired at different positions along the NW lengths in the seven regions indicated in the TEM

image of Fig. 10b. Eu emission at 622 nm is clearly observed within the first 1000 nm from the top. This is in good agreement with the Monte Carlo simulations showing that most Eu ions come to rest in this region for high NW density. At the bottom part of the NW only broader bands at ~400 and ~570 nm are observed. Emission at 400 nm was also observed in PL spectra of the as-grown samples and attributed to donor acceptor pair transitions while the yellow emission was formed after implantation/annealing and attributed to defects[8]. In the present case, the yellow luminescence in spectra 5, 6 and 7 may be due to defects created by sputtered atoms or surface defects created during annealing. Figs. 10c and d show maps of the luminescence intensity from the same NW integrating the region from 350 to 550 nm (Fig. 10c), corresponding mainly to DAP emission, and integrating only the Eu^{3+} emission line at 622 nm (Fig. 10d). These maps clearly show that Eu-emission is mainly observed at the top of the NWs. Fig. 10e presents a more detailed luminescence map of the Eu^{3+} emission within a region corresponding to the highest Eu concentration (marked with the larger green rectangle in Fig. 10b). Lower Eu^{3+} emission intensity is observed at the NW edges due to both a lower probed sample volume and low Eu concentration at the surface. Even when disregarding the edges, Eu^{3+} emission intensity fluctuations at the nanoscale are visible. Each pixel in the map corresponds to an area of 10x10 nm^2. Taking into account the nanowire density, dimension and the fluence, the number of Eu ions can be roughly estimated to be some tens of ions per pixel. The spatial fluctuations of emission intensity can be explained by the facts that only a small fraction of Eu ions are optically active[55,56] as well as by the long lifetimes of the excited Eu^{3+} states leading to a long "dark-time" of individual ions. Furthermore, as mentioned above, ions may be incorporated into sites which do not promote optical activity e.g. due to a valence state different from 3+.

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4. Eu incorporation

Eu and other rare earth ions in GaN thin films are known to be preferentially incorporated in substitutional Ga-sites or slightly displaced from that site[6,55,57,58,59,60]. Experimentally this was shown by ion channeling or emission channeling techniques which cannot be easily applied to NWs due to the low critical angles for dechanneling which are in the order of the tilt angles between individual NWs. Therefore, here we apply X-ray absorption techniques to assess the incorporation site and valence state of implanted Eu ions in NWs and thin films. Indeed, EXAFS has been successfully applied in Eu implanted and in situ doped GaN films[61,62]. The nanoscopic nature of X-ray absorption techniques, being sensitive only to a few atomic neighbor shells around the probe atom, is ideal for the comparison of bulk material and nanostructures. A more detailed description of the data analysis can be found in the supplementary material.

Figure 11 presents the absorption spectra near the Eu L_{III} edge (X-ray absorption near edge structure (XANES) part only) for various thin film (Fig. 11a) and NW (Fig. 11b) samples after annealing. All spectra exhibit two contributions to the absorption edge corresponding to the Eu^{2+} white line at fixed energy position 6975.3±0.3 eV while the line for Eu^{3+} varies from 6981.5 to 6983.1 eV. This is most visible for the thin film sample implanted with a fluence of 1×10^{15} at/cm^2 (RTA at 1000 °C) with Eu^{2+} and Eu^{3+} fractions of 33% and 67%, respectively. Coexistence of Eu in 2+ and 3+ oxidation states has also been reported for Eu-doped ZnO nanowires[63]. In contrast to GaN, in the case of ZnO substitutional Eu is expected to reside in the 2+ charge state but interaction with intrinsic defects allows the stabilization in the 3+[64],[65].

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We observe that the Eu^{2+} contribution decreases when the fluence is lowered to 5×10^{14} at/cm^2 and becomes hardly visible for the HTHP annealed reference sample implanted to a fluence of 1×10^{14} at/cm^2, which shows an Eu^{2+} fraction of only 16%. A low Eu^{2+} fraction of 18% is also seen for NW samples implanted to a fluence as high as 1×10^{15} at/cm^2 provided they are implanted at 600°C. As the high implantation temperature promotes defect mobility during the implantation, this can lead to annihilation of defects or to increased interaction of defects among each other.

XANES measurements for Eu implanted directly in Si, SiO_2 and Si_3N_4 wafers revealed that Eu in these materials is incorporated entirely in the 2+ charge state (see supplementary material); as implantation of GaN NWs at 600 °C results in more than 80% of Eu^{3+}, this is coherent with nano-CL results which suggested that Eu does not reach the Si substrate. Consequently, the presence of Eu^{2+} in GaN seems to be correlated to the presence of residual implantation defects after annealing.

However, the correlation of defect density and Eu^{2+} fraction is not straightforward. As can be seen in Fig. 11 a and b, the Eu^{2+} fraction is decreasing with further increase of fluence above 1×10^{15} at/cm^2 for both NW and thin film samples although the residual defect density should be higher for these high fluence implantations. This complex behavior shows that not simply the overall defect concentration is decisive for the Eu charge state but also the exact defect arrangement and nature around the Eu ion.

It is interesting to mention that the irradiation of as-implanted (not annealed) samples with X-rays leads to the photo-oxidation of Eu^{2+} to Eu^{3+} which induced an Eu^{3+}/Eu^{2+} ratio increase of up to 40% in 7 hours (see supplementary material for further details). For the highest fluence of 5×10^{15} at/cm^2, directly after the implantation, the fraction of Eu^{2+}

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

is as high as 31% for thin films and 44% for NWs, and reduces after annealing to 13 and 22%, respectively. Analogously, thermal annealing leads to conversion of Eu^{2+} to Eu^{3+}. The increasing Eu^{3+}/Eu^{2+} ratio, caused either by thermal annealing or X-ray irradiation, is accompanied by a better defined EXAFS signal revealing a more ordered environment around Eu suggesting annealing of defects. Therefore, we concentrated our further investigation on annealed samples where, within the duration of the EXAFS measurement, no changes were seen for the case of NWs and only moderate changes for thin film samples.

Inspecting the shape of the XANES curves in Fig. 11, there is a clear evolution when decreasing the implantation fluence with a shift of the Eu^{3+} absorption edge to a lower energy and a third feature occurring at the high energy side of the Eu^{3+} white line. Such a change is most likely related with a local change of the Eu nearest neighbors' coordination. This interpretation is also supported by the EXAFS results shown in Fig. 12 (for a detailed description of the EXAFS data analysis see the supplementary material).

Fig. 12 shows the Fourier transforms of the EXAFS spectra and fits for NW and thin film samples implanted to different fluences after annealing at 1000 °C as well as the thin film reference after HTHP annealing at 1400 °C. Qualitatively the results are very similar for NWs and thin films. For the highest fluence, only the first neighbor shell (lowest R bump around pseudo-radius R=2 Å) is visible and corresponds to light atoms, presumably nitrogen. The second neighbor shell (expected around pseudo-radius R=3 Å) is not visible suggesting that Eu and N in the 1st shell form a locally ordered complex while the distortion of the crystal due to the oversized Eu (compared to Ga) and due to implantation defects prevents a well ordered crystal structure of the 2nd shell and

beyond. With decreasing fluence and therefore decreasing defect density, intensity of the first shell decreases, i.e. the number of N atoms in the 1st neighbor shell is reduced, while the 2nd neighbor shell intensity - consisting of Ga atoms - becomes increasingly visible thus revealing the ordering of the crystal structure around Eu.

Detailed data fitting allows further interpretation of this data. Starting with the low fluence HTHP annealed reference layer, the $|\chi(R)|$ graph (see Fig. 12a) reveals at least 8 well defined surrounding shells below 6 Å with a maximal intensity on the second shell at pseudo-radius R=3 Å. This demonstrates that the Eu local environment is of very good crystalline quality, dominated by a second shell of heavy elements. A good fit is obtained assuming 100% of the Eu incorporated on substitutional Ga-sites, i.e. with 4 nitrogen atoms as nearest neighbors, 12 Ga-atoms in the second, 10 N-atoms in the third and 6 Ga atoms in the fourth neighbor shells. The first neighbor shell is strongly distorted (by ~11% with an Eu-N nearest neighbor distance of 2.15 Å compared to a Ga-N nearest neighbor distance of 1.94 Å in pure GaN) as expected, due to the large effective ionic radius of Eu^{3+} (linearly estimated to 83.5 pm) compared to Ga^{3+} (61 pm) in tetrahedral environment[66] and in good agreement with previous studies on rare earth doped GaN and other III-N alloys[61,62,67,68]. The more distant shells are found close to the expected positions in undisturbed GaN (with a Eu-Ga next-nearest neighbour distance of 3.17 Å compared to a Ga-Ga nearest neighbor distance of 3.18 Å in GaN). Debye-Waller factors are small ($<5\times10^{-3}$ Å^{-2} for all shells) revealing a good crystal quality. The strongly dilated first neighbor shell would allow for the incorporation of more than 4 nitrogen atoms and indeed leaving the number of next nearest neighbors as free fitting parameter yields 5.3+/-1.9 N as first shell without changing the goodness of the fit. It should be noted, that a contribution of oxygen on the 1st nearest neighbor site cannot be discarded.

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The graph for the lowest fluence in NWs looks qualitatively similar (see Fig. 12b) but cannot be fitted assuming 100% of undisturbed substitutional Eu. The simplest model able to satisfactorily fit the data of all samples consists of two fractions of Eu: the first fraction corresponding to undisturbed substitutional sites, Eu_{Ga}, and the second fraction (dominant for higher fluences and in the following named EuN-like fraction) characterized by a local arrangement consisting of more than 4 nitrogen atoms at a distance of ~2.5 Å, that is considerably larger than for Eu_{Ga} but similar to the Eu-N distance in EuN which is 2.51 Å[69]. Details of the fit results are given in the supplementary material. The main conclusion is illustrated in Fig. 13 showing the fraction of substitutional Eu_{Ga} as a function of the fluence for all analyzed samples. The substitutional fraction is seen to decrease with implantation fluence and is typically lower for NW samples than for thin film samples. For the highest fluence in thin films and NWs this fraction approaches zero and all Eu ions are found in EuN-like environment. The figure shows furthermore that the as-implanted NWs (1×10^{15} at/cm^2) show slightly higher substitutional fractions than after annealing which is consistent with ion channeling data on ion-implanted thin films and probably due to defect diffusion and trapping during annealing[53].

Although the 1×10^{15} at/cm^2 (RTA @1000 °C) NW sample implanted at 600 °C reveals a higher Eu^{3+}/Eu^{2+} ratio than for implantation at room temperature the Eu_{Ga} substitutional fraction drops to zero. The higher mobility of defects during implantation at elevated temperatures seems to favor the formation of EuN-like complexes. This is consistent with the XANES spectral shape which resembles that of high fluence implanted samples (see Fig. 11).

On first sight, the change of preferential incorporation site from Eu_{Ga} for low fluences to EuN-like for high fluences might seem contradicting to the optical data showing similar spectral shapes for all samples. This discrepancy shows once more that only a small fraction of Eu is optically active while in EXAFS we probe the majority sites. This interpretation is consistent with the slow increase/saturation of Eu-luminescence intensity in NWs and the decrease in thin films (see Fig. 9).

CONCLUSIONS

GaN NWs and thin films were implanted with Eu ions in a fluence range from 1×10^{13} at/cm^2 to 5×10^{15} at/cm^2. The distribution of Eu inside the NWs can be tuned by adapting the NW diameter, density and implantation conditions as shown by Monte Carlo simulations. Implantation damage was assessed by XRD revealing considerably lower strain introduced by implantation defects in NWs than in thin films implanted in the same condition. In good agreement, and despite a high level of surface defects, the NW core is shown to be of high crystal quality for fluences as high as 1×10^{15} at/cm^2 and after annealing. The formation of extended defects and defect clusters is suppressed compared with implantation studies in GaN thin films. Optical activation of Eu^{3+} is achieved upon annealing with similar optical centers in NWs and thin films. For the case of NWs the CL emission intensity increases within the entire fluence range, while it saturates or even decreases at higher fluences for the case of thin films suggesting stronger luminescence quenching due to implantation defects in thin films. Eu ions coexist in 2+ and 3+ charge state although Eu^{2+} can be almost suppressed by optimizing the implantation and annealing conditions. The local lattice environment of Eu is similar

in NWs and thin films, however, in both cases it is strongly distorted by implantation defects and the oversized Eu ion. In particular, for high fluences, EXAFS only shows a signal from the first neighbor shell and suggests that a large fraction of Eu resides in a EuN like configuration. For lower fluences and more efficient annealing techniques, EXAFS results are consistent with a substitution of Ga by Eu. This transition from an EuN to a GaN:Eu_{Ga} like structure occurs at lower fluences for NWs than for thin films suggesting that the EuN like structure forms more easily in NWs. The presented results help to establish guidelines for the use of ion implantation as processing tool for GaN nanostructures. In particular, and despite the successful optical activation of Eu in all samples, high fluences should be avoided due to severe surface damage and the formation of local EuN-like structures.

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SUPPORTING INFORMATION

Details of the dynamic Monte Carlo simulation

Details on XAS analysis:

- Eu charge state in GaN and changes of the XANES signal with X-ray irradiation

- Eu charge state in Si, SiO_2 and Si_3N_4

- EXAFS signal analysis

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FIGURES

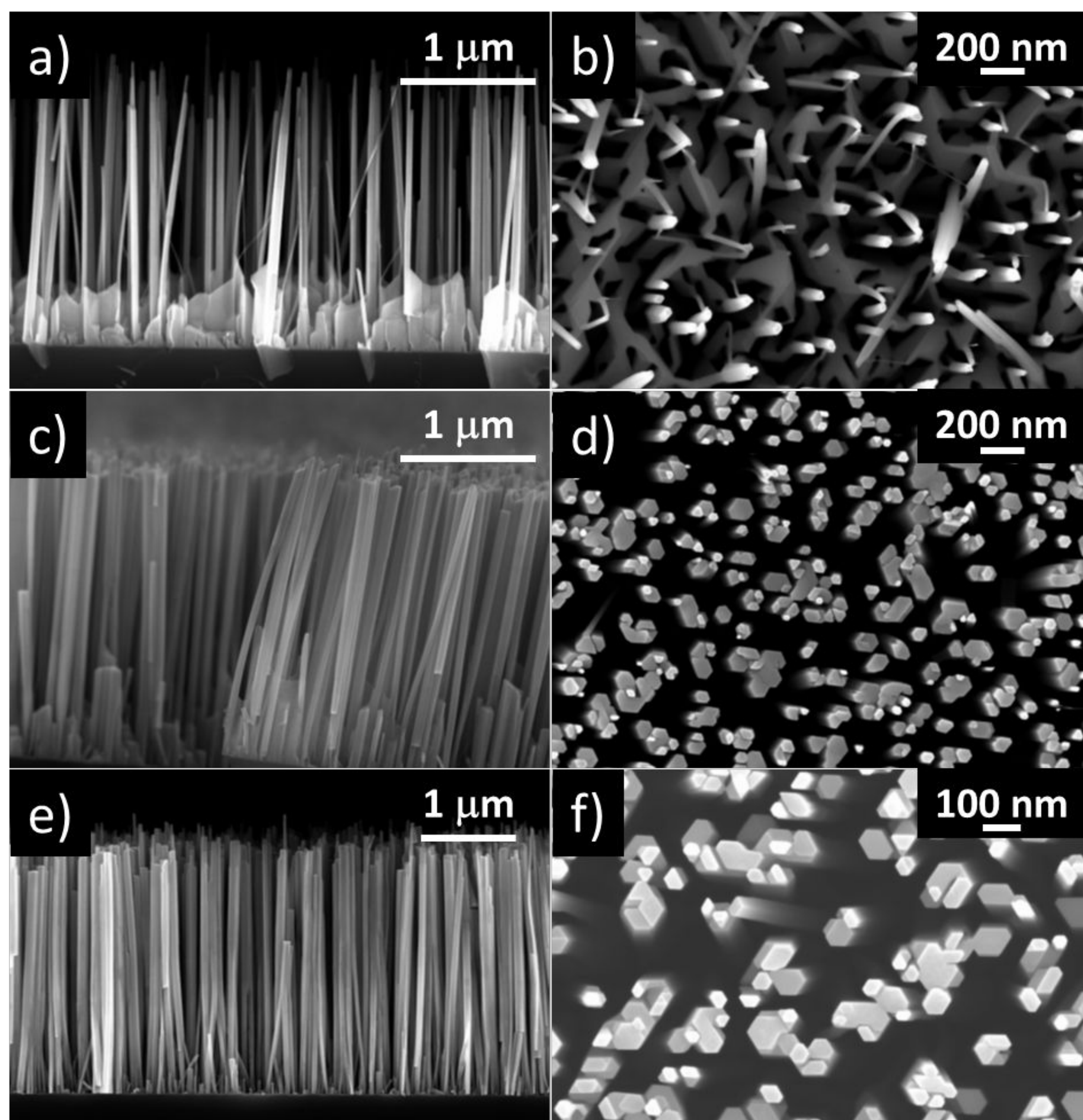

Fig. 1: SEM side-view and top view images of the nanowires used for XRD, TEM and CL analysis (set 1) corresponding to the wafer centre (a and b) and to the wafer periphery (c and d). e) and f) show typical SEM images of the NWs used for XANES and EXAFS analysis (set 2).

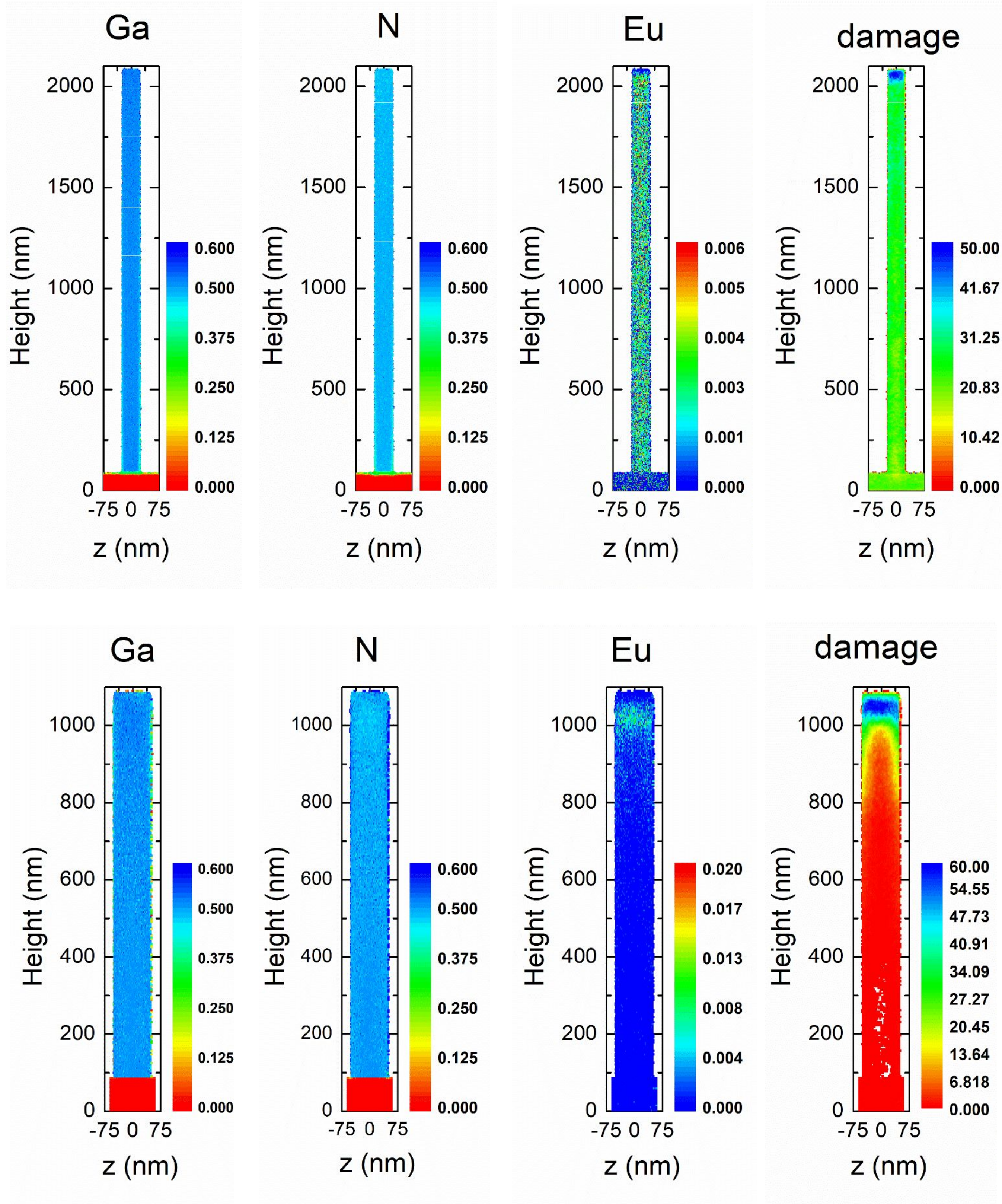

Fig. 2: TRI3DYN simulation results showing the elemental distribution of Ga, N and Eu as well as the damage distribution (in dpa) in a longitudinal slice of 8 nm thickness along

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the NW length. Top: for an array of 50 nm diameter NWs with an areal density of 2×10^9 cm^{-2}; Bottom: for an array of 100 nm diameter and an areal density of 7×10^9 cm^{-2}.

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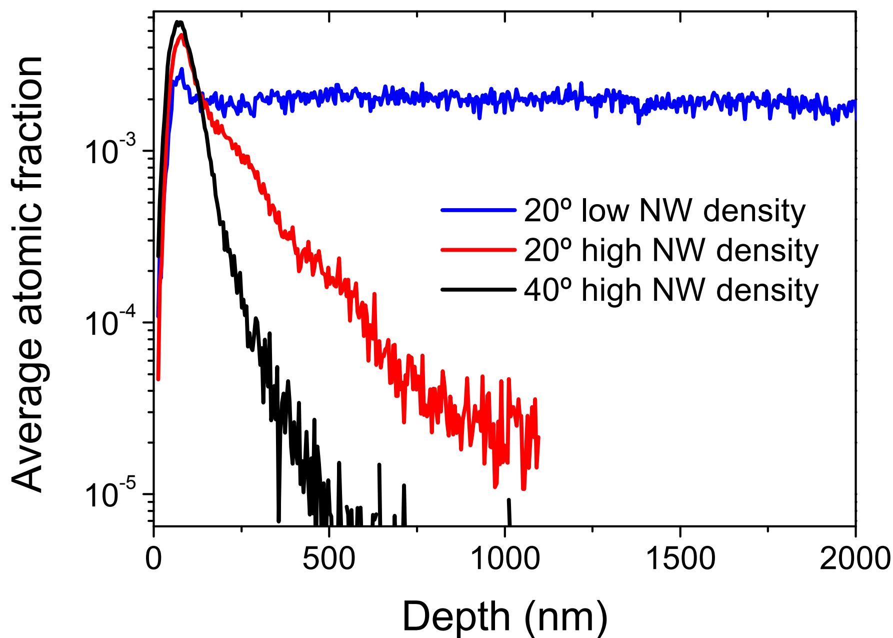

Fig. 3: TRI3DYN simulation results showing the average atomic Eu fraction along the NW length for the three combinations of implantation angle, NW diameter and density.

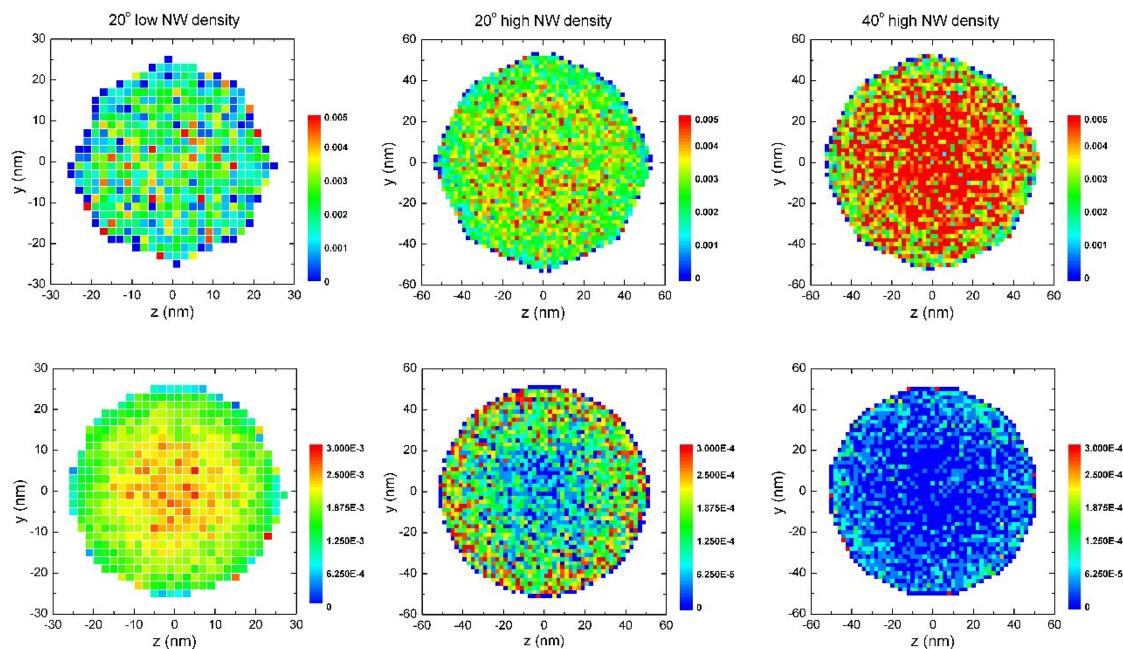

Fig. 4: TRI3DYN simulation results showing the lateral distribution of Eu for the three combinations of implantation angle, NW diameter and density. Top: The data was integrated close to the tip of the NW corresponding to the end of range of ions entering the NW from the top. Bottom: The data was integrated from ~50-150 depth until the NW base in order to disregard ions that entered the NWs from the top surface.

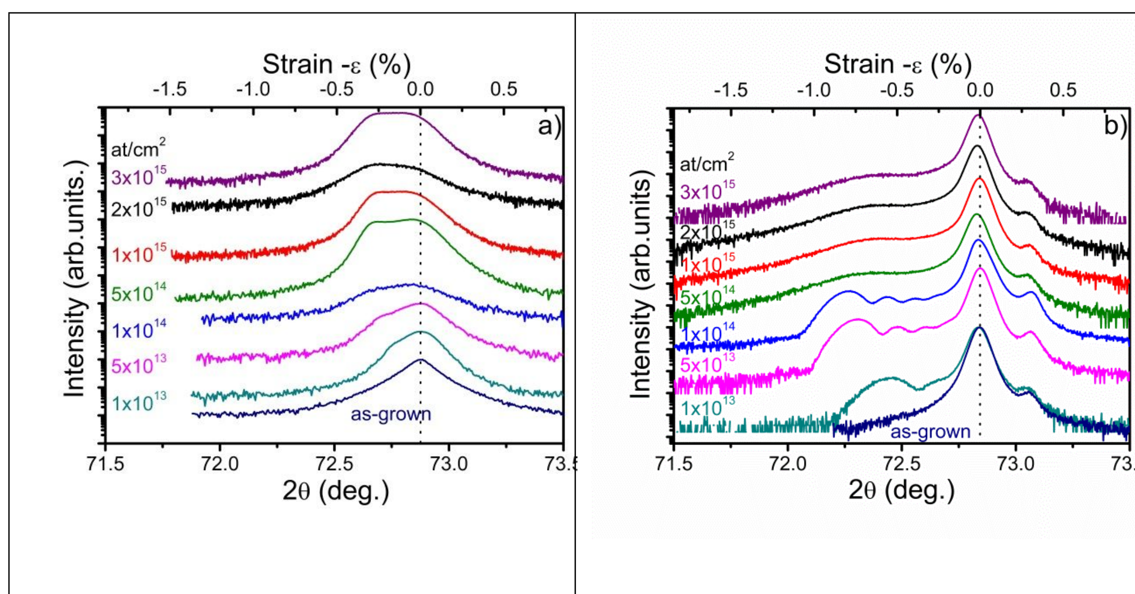

Fig. 5: XRD (0004) 2θ–θ curves for the first set of NWs (a) and reference thin films (b) implanted to different fluences at 20° incidence. Note that the small peak at ~73.1° visible in b) is an artefact of the XRD system due to the incomplete suppression of the $CuK_{\alpha 2}$ line.

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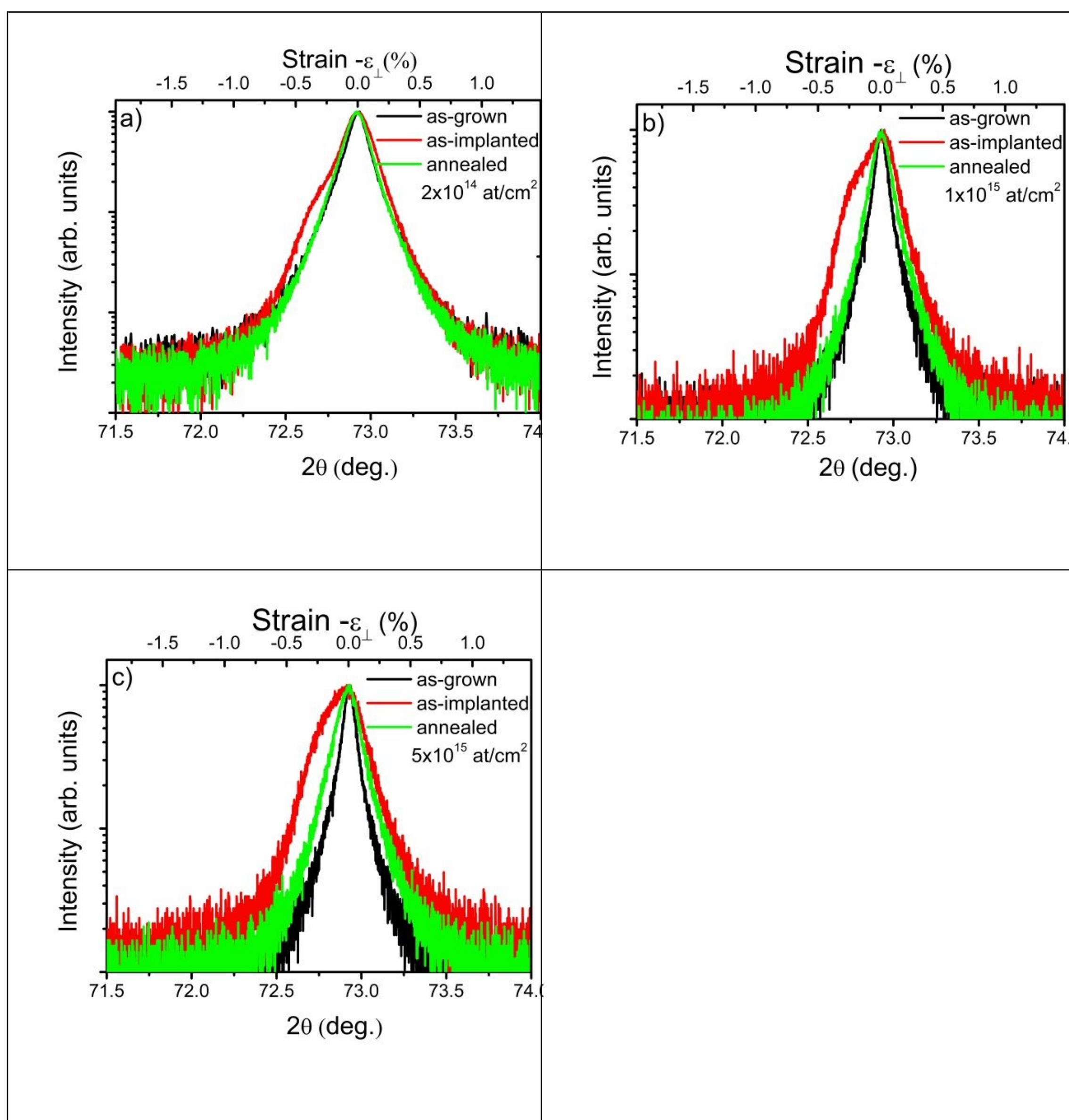

Fig. 6: XRD 2θ–θ curves of high density GaN NWs implanted with 40° tilt comparing as-grown, as-implanted and annealed samples implanted to fluences of 2×10^{14} at/cm^2 (a) 1×10^{15} at/cm^2 (b) and 5×10^{15} at/cm^2 (c).

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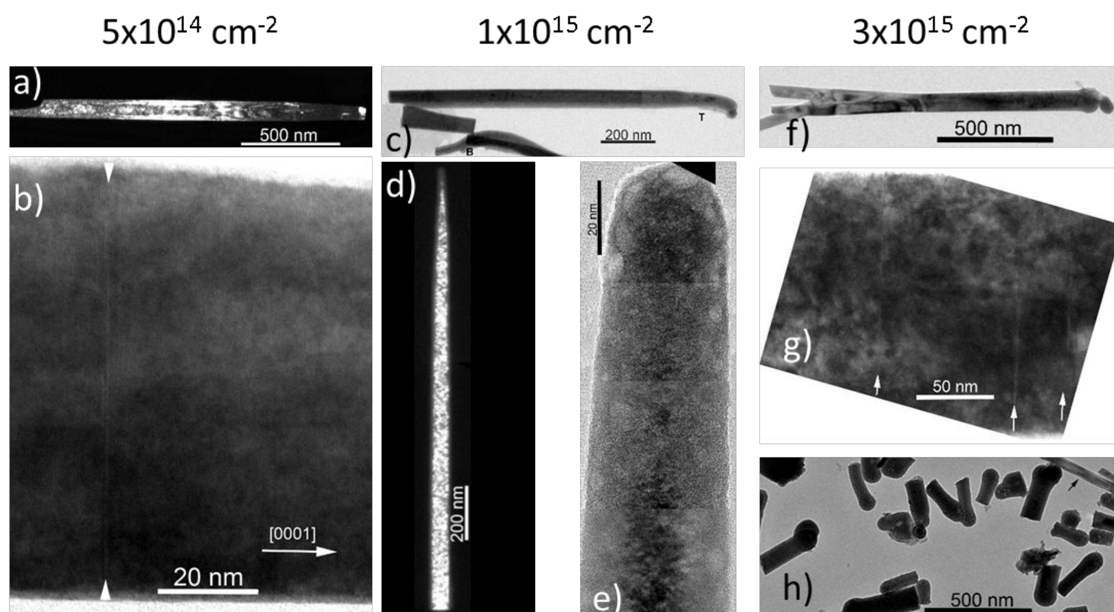

Fig. 7: TEM images of as-implanted NWs implanted to a fluence of 5×10^{14} cm^{-2} (a,b), 1×10^{15} cm^{-2} (c-e) and 3×10^{15} cm^{-2} (f-h). Basal stacking faults are marked by white arrows.

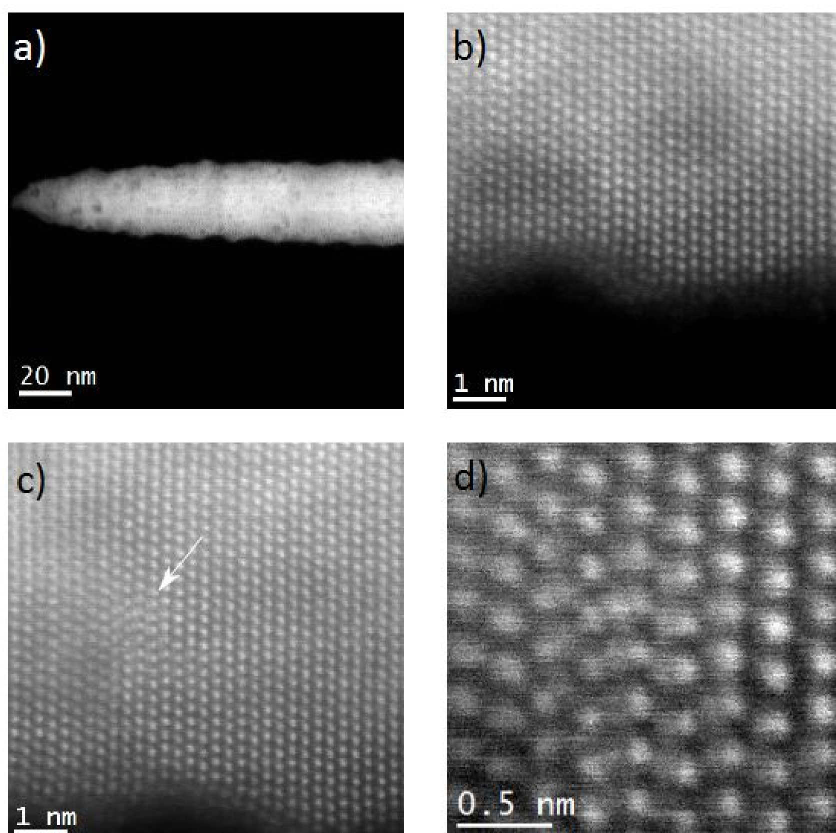

Fig. 8: a) STEM HAADF image of a NW implanted to a fluence of 1×10^{15} at/cm^2 and annealed at 1000 °C. b) - d) High resolution STEM HAADF images of the same NW showing high crystalline quality of the NW core (b) and an isolated extended defect (c and d).

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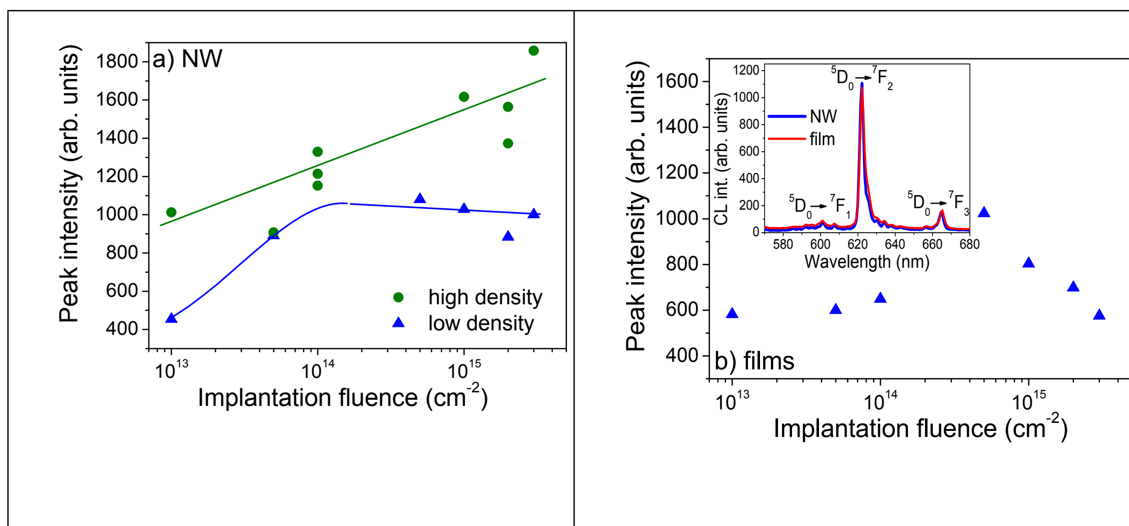

Fig. 9: RT CL peak intensity of the Eu^{3+} emission line at ~622 nm as a function of the fluence for NWs in regions with low and high NW density (a) and thin film reference samples (b). The inset in b) compares typical CL spectra for NW and thin film samples.

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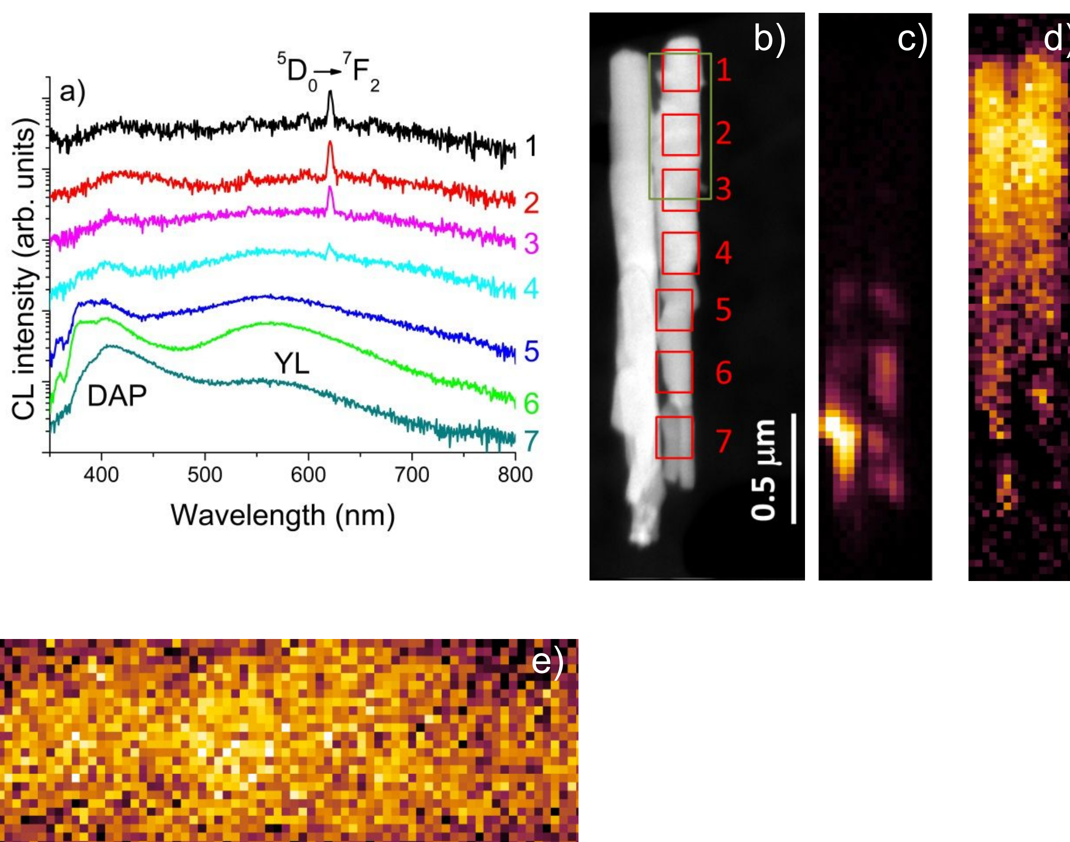

Fig. 10: a) Nano-CL spectra taken at seven points from the top (1) to the bottom (7) of a single NW implanted to a fluence of 1×10^{14} at/cm^2 (20° incidence angle) and annealed at 1000 °C. The regions at which the spectra were taken are indicated with red rectangles in (b). c) and d) Luminescence intensity maps integrating the spectra in a wavelength region from 350 to 550 nm (c) and around the 622 nm Eu^{3+} line (d). e) Detail of the luminescence intensity map integrating the Eu^{3+} emission peak at 622 nm in the region with highest Eu-emission marked with the bigger green rectangle in b); the pixel size is 10×10 nm^2.

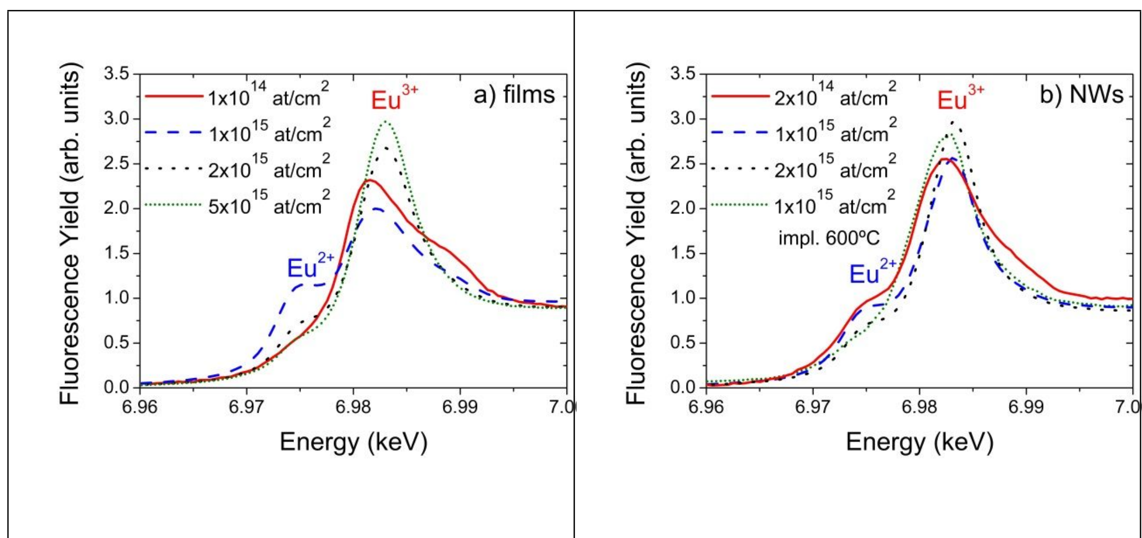

Fig. 11: XANES spectra for selected thin films (a) and NWs (b) showing the coexistence of Eu in the 2+ and 3+ charge state and the possibility of decreasing the Eu^{2+} fraction by HTHP annealing or implantation at elevated temperature plus RTA at 1000 °C. The Eu^{2+} edge is found at a fixed position in all samples while the position of the Eu^{3+} varies slightly for different implantation/annealing conditions.

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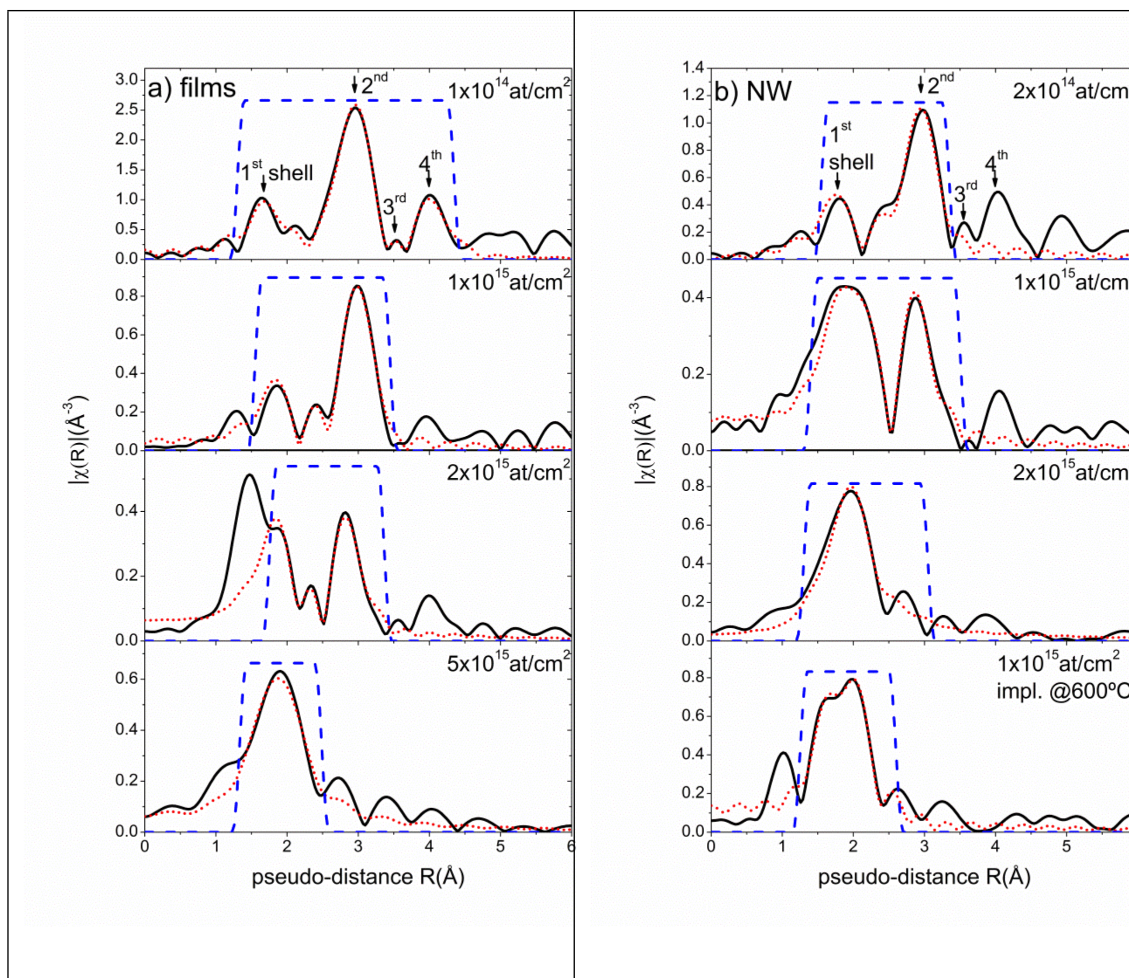

Fig. 12: Fourier transform of the EXAFS signal and fits of selected films (a) and NWs (b) showing the experimental data (black solid line), the fit (red dotted line) and the window used to do the fit (blue dashed line). Note that in thin film sample 2×10^{15} at/cm^2, the low-R bump is an artefact arising from a baseline residual oscillation that could not be suppressed.

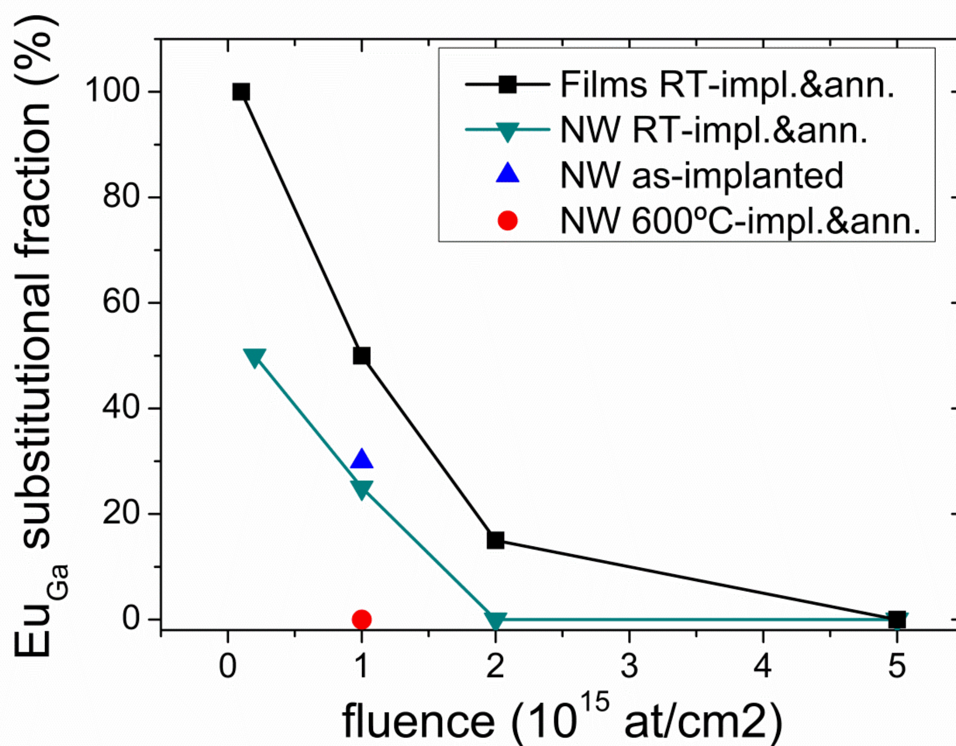

Fig. 13: Fraction of Eu incorporated in substitutional Ga-sites as a function of the fluence for thin film and NW samples in different conditions as given in the legend. RT-impl.: implanted at RT; 600 °C-impl.: implanted at 600 °C; ann: annealed at 1000 °C except for the thin film sample implanted to 1×10^{14} at/cm^2 which was annealed at 1400 °C.

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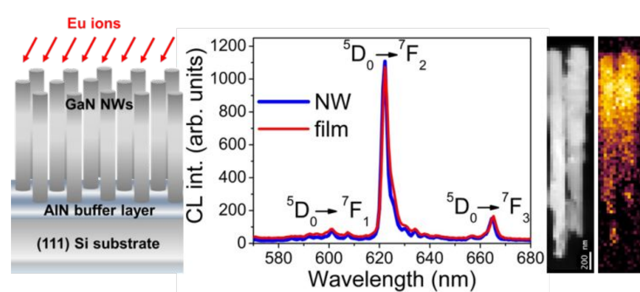

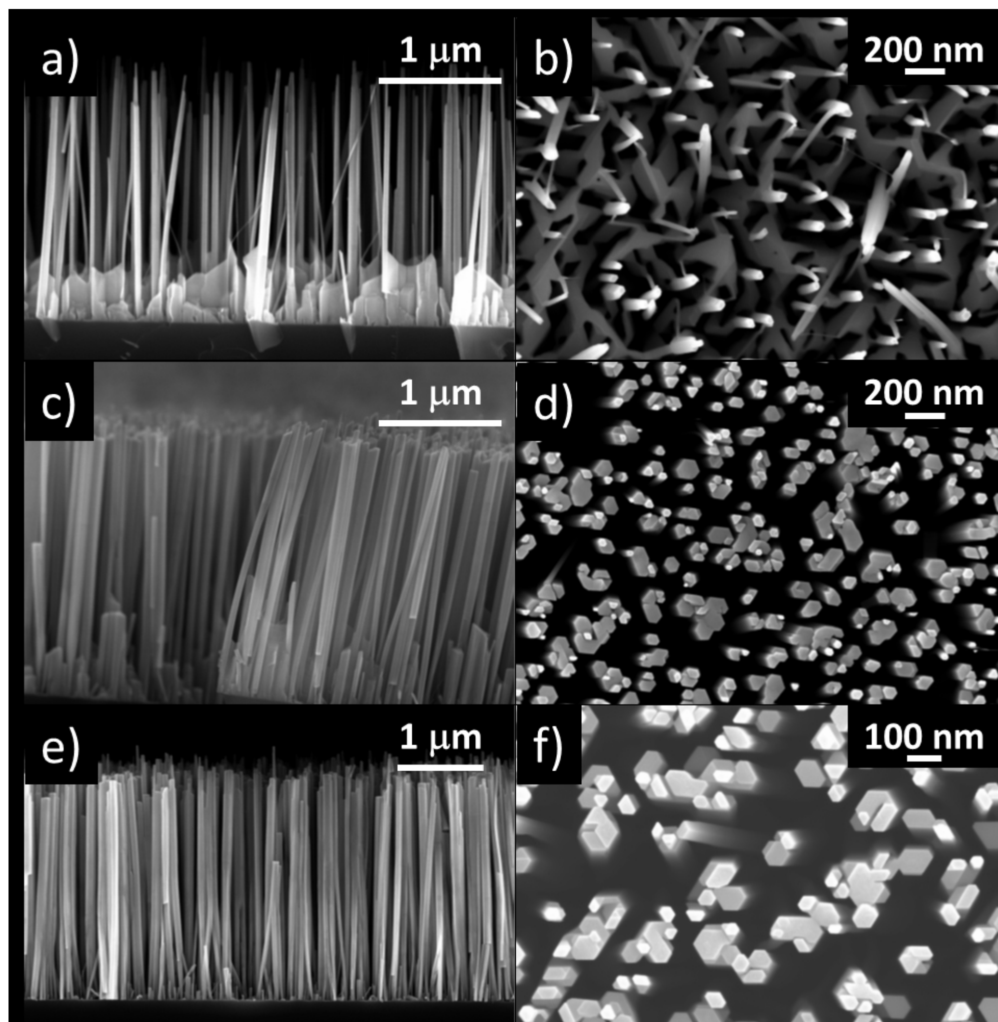

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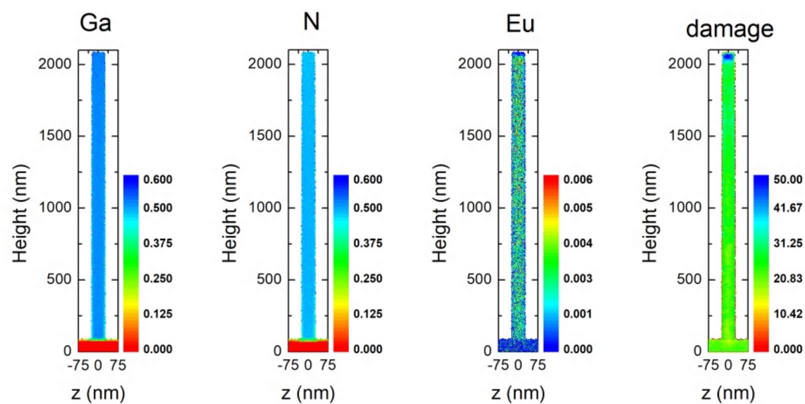

287x202mm (300 x 300 DPI)

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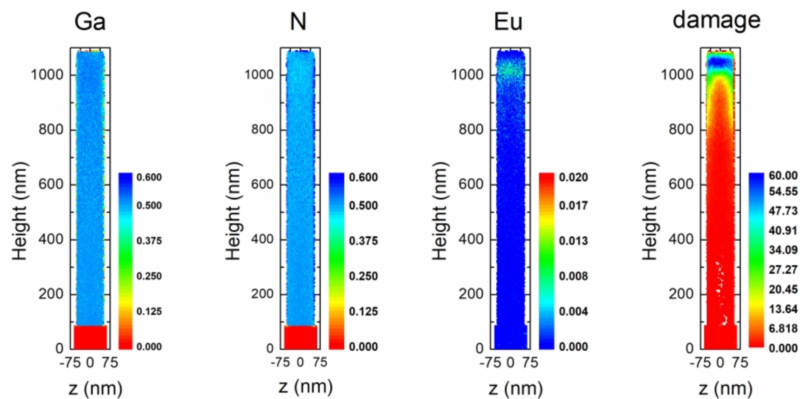

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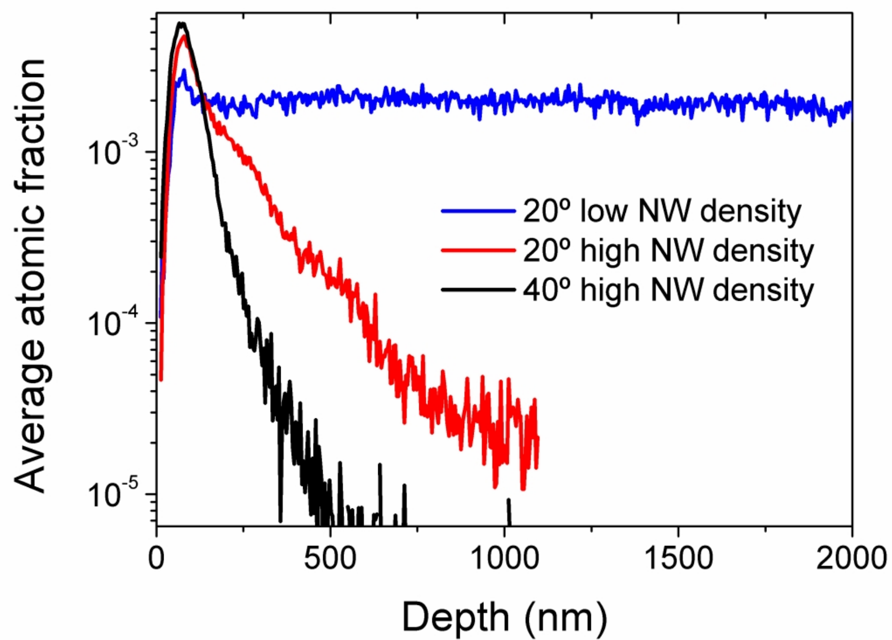

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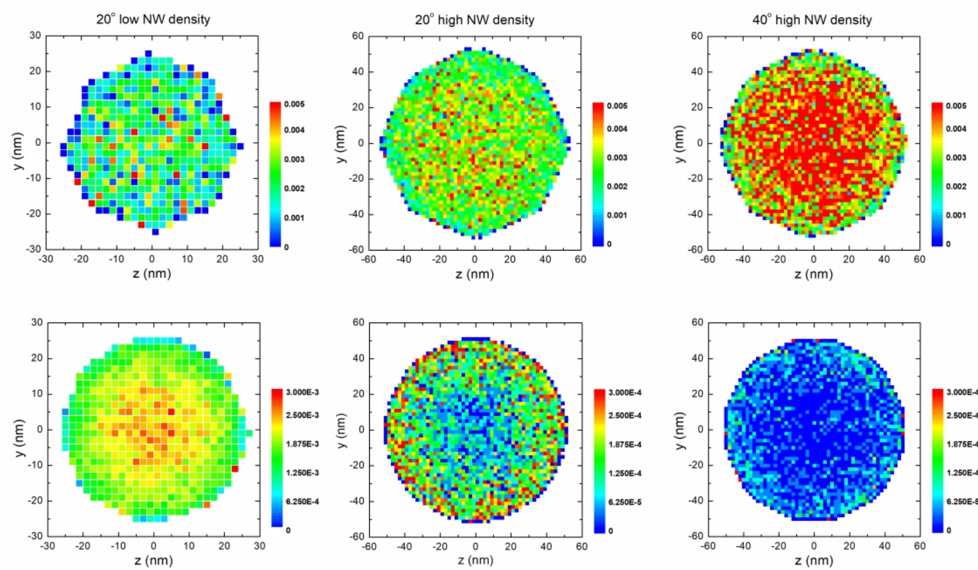

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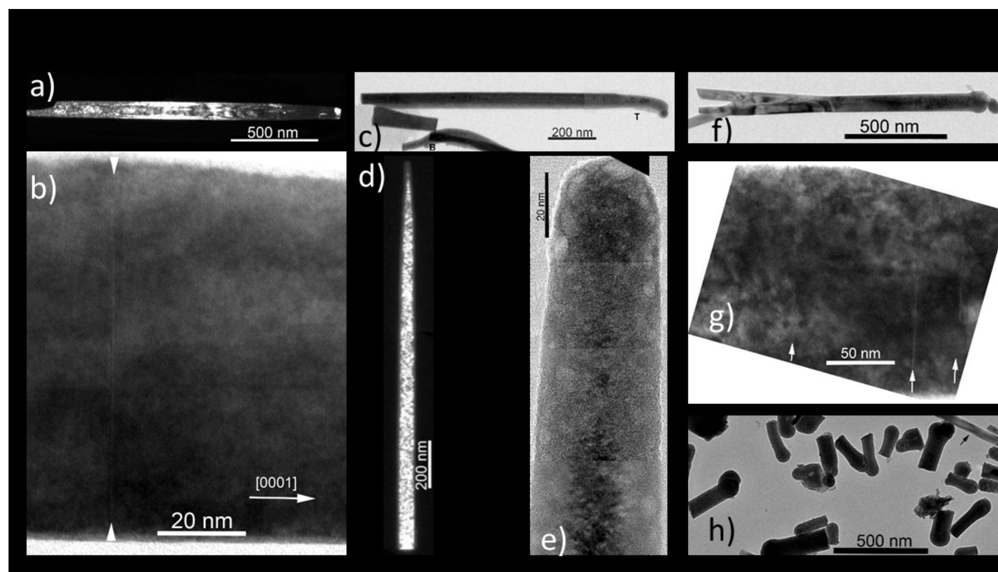

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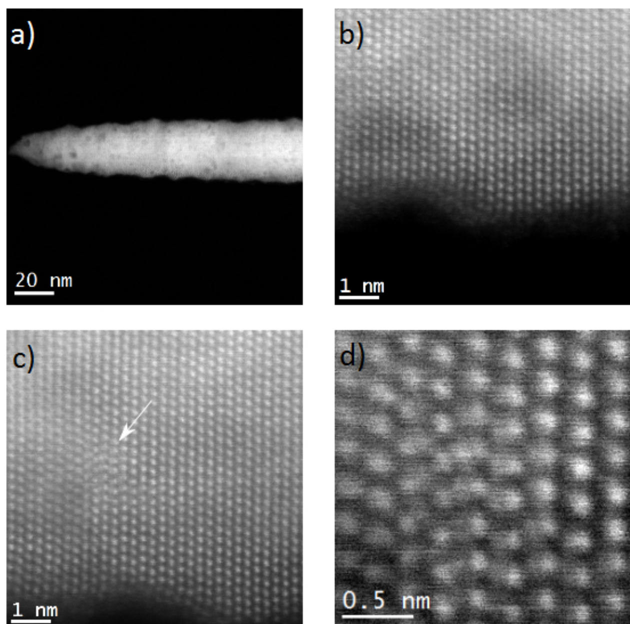

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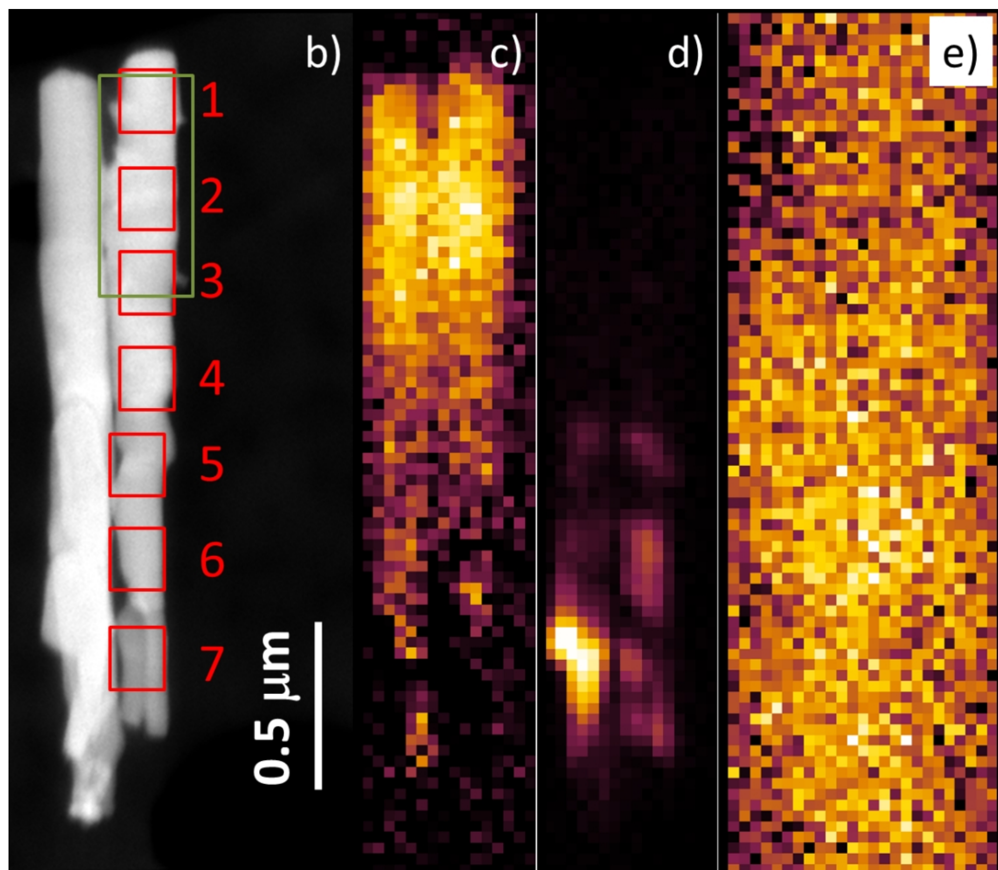

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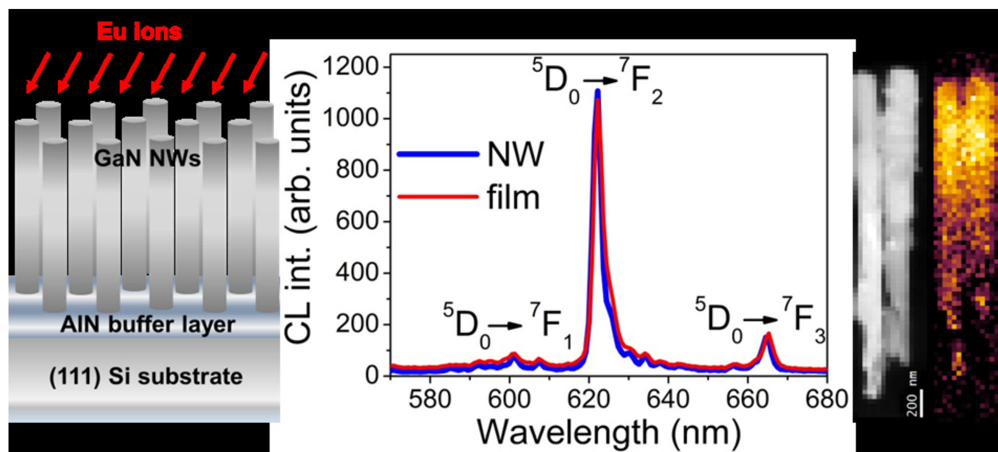

161x71mm (150 x 150 DPI)