Incorporation of Mn in Al$_x$Ga$_{1-x}$N probed by x-ray absorption and emission spectroscopy, high-resolution microscopy, x-ray diffraction and first-principles calculations

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Synchrotron radiation x-ray absorption and emission spectroscopy techniques, complemented by high-resolution transmission electron microscopy and density functional theory calculations are employed to investigate the effect of Mn in Al$_x$Ga$_{1-x}$N:Mn samples with an Al content up to 100%. The atomic and electronic structure of Mn is established together with its local environment and valence state. A dilute alloy without precipitation is obtained for Al$_x$Ga$_{1-x}$N:Mn with Al concentrations up to 82%, and the surfactant role of Mn in the epitaxial process is confirmed.

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INTRODUCTION

Hetero-structures based on III-nitrides [1] and in particular on the combination Al$_x$Ga$_{1-x}$N/GaN represent the basis of a variety of state-of-the-art (opto)electronic devices like blue and white light-emitting diodes [2], laser diodes [3], blue lasers [4], high-power- [5], and high-electron-mobility-transistors [6]. Most of the above mentioned devices are commercially available and their performance continuously improved. Furthermore, III-nitrides doped with transition metals (TM) have also been the focus of considerable research efforts towards the demonstration of semiconductor spintronic functionalities [7]. In this respect, while a remarkable number of reports on GaN:Mn provide an overview on the structural, optical, magnetic and electric properties of this material system [8–15], little is known about Al$_x$Ga$_{1-x}$N:Mn [16–19] and related nanostructures [20]. Recent findings [21] indicate this alloy as particularly interesting for e.g. the self-assembly of functional multilayers and for having revealed the decisive role of Mn as surfactant during the epitaxial growth of Al$_x$Ga$_{1-x}$N:Mn, considerably enhancing the critical thickness of Al$_x$Ga$_{1-x}$N:Mn on GaN, and opening new perspectives for the realization of e.g. improved reflectors in GaN-based laser structures. We report here on Al$_x$Ga$_{1-x}$N:Mn grown by means of metalorganic vapor phase epitaxy (MOVPE) in a broad range of Al concentrations and extensively investigated via x-ray absorption spectroscopy (XAS), x-ray emission spectroscopy (XES), energy-dispersive spectrometry (EDS), x-ray diffraction (XRD), and high-resolution (HR) transmission electron microscopy (TEM), supported by density functional theory (DFT) calculations. The results provide fundamental information on the microstructure and local environment in the layers and on the valence state of Mn incorporated in the lattice over the whole range of Al concentrations.

EXPERIMENTAL AND THEORETICAL METHODS

The wurtzite (wz) Al$_x$Ga$_{1-x}$N:Mn samples are grown in an AIXTRON 200RF horizontal-tube MOVPE reactor. All structures are deposited on c-plane sapphire substrates with trimethylgallium (TMGa), trimethylaluminum (TMAI), bis-methylcyclopentadienyl-manganese (MeCp$_2$Mn) and ammonia (NH$_3$) as precursors for respectively Ga, Al, Mn, N, and with H$_2$ as carrier gas. The epitaxial process, developed from a well established procedure [22], consists of: (i) substrate nitridation; (ii) low temperature (540 °C) deposition of a GaN nucleation layer (NL); (iii) its annealing under NH$_3$; (iv) growth of a 1 µm device-quality GaN buffer deposited at 1020 °C; (v) Al$_x$Ga$_{1-x}$N:Mn layers at 850 °C, with the same TMGa and MeCp$_2$Mn flow rates and different - over the sample series - TMAI flow rates ranging from 1 to 80 standard cubic centimeters per minute (sccm). In order to have real time control over the entire fabrication process, the MOVPE system is equipped with an in situ Isa Jobin Yvon ellipsometer that allows for both spectroscopic and kinetic measurements in the energy range 1.5 – 5.5 eV [23]. The structures are routinely characterized by atomic force microscopy (AFM), secondary-ion mass spectroscopy (SIMS) and (magneto)photoluminescence (PL) and SQUID magnetometry in order to get information on the surface roughness, chemical composition, magnetic and magnetooptical response, respectively. Here, we focus on the effect of Mn incorporation on the structural arrangement of Al$_x$Ga$_{1-x}$N:Mn and on the local atomic environment of Mn, with particular attention devoted to the XRD and HRTEM analysis as essential complement to the synchrotron XAS and XES measurements. All considered Al$_x$Ga$_{1-x}$N:Mn samples are listed together with their growth parameters in Table I. The Mn concentration in all doped layers is ~1% cations, as established by SIMS analysis.

High resolution XRD measurements are carried out in a
TABLE I. Growth parameters for the Al$_x$Ga$_{1-x}$N:Mn samples presented in this work. Al concentration $x$ (from XRD); TMGa and TMAI flow rates and the pressure $P$ in the reactor during the process. The MeCp$_2$Mn and NH$_3$ flow rates are fixed at 490 sccm and 1500 sccm, respectively; the substrate temperature during the growth of the GaN buffer layer and during the deposition of the Al$_x$Ga$_{1-x}$N:Mn layer are, respectively, 1020 °C and 850 °C. The nominal thickness is obtained from the kinetic ellipsometry spectra and confirmed by TEM cross-sections.

| sample | $x$ | TMGa | TMAI | $P$ | thickness |
|--------|-----|------|------|-----|-----------|
| #A     | 12% | 1    | 1    | 100 | 260       |
| #B     | 20% | 1    | 3    | 100 | 293       |
| #C     | 41% | 1    | 9    | 100 | 377       |
| #D     | 59% | 1    | 27   | 100 | 553       |
| #E     | 71% | 1    | 80   | 100 | 845       |
| #F     | 82% | 1    | 80   | 50  | 780       |
| #G     | 100%| 0    | 80   | 100 | 553       |

The x-ray absorption and emission measurements at the Mn K-edge (6539 eV) are carried out at the beamline ID26 at the European Synchrotron Radiation Facility (ESRF). The incoming x-ray beam, linearly polarized in the horizontal plane, is produced by three coupled undulators and the flux of $\sim 10^{13}$ ph/s on the sample. The measurements are carried out in fluorescence mode at room temperature and under nitrogen flow to avoid depositing ambient impurities on the samples’ surface. The total fluorescence yield (TFY) spectra are obtained with a Si photodiode, while the high energy resolution fluorescence detected (HERFD) spectra are acquired with a wavelength dispersive spectrometer equipped with 5 spherically bent crystal analyzers and an avalanche photodiode arranged in a vertical point-to-point Rowland circle geometry [25]. The HERFD-XAS data are collected at the maximum of the K$_{\alpha}$ emission line using Ge(333) analyzers. The XES measurements are performed at the K$_{\beta}$ core-to-core lines (K$_{\beta}^\prime$ and K$_{\beta,1,3}$) using Si(440) analyzers and with the incoming excitation set at 6700 eV. For these configurations, the total energy resolutions (monochromator plus spectrometer) are, respectively, $\sim$1.3 eV and $\sim$1.0 eV (full-width-at-half-maximum). In addition, to exploit the natural linear x-ray dichroism (XLD) arising from the wurtzite hexagonal lattice [26], two geometries are employed: the vertical grazing incidence (VGI) and the horizontal grazing incidence (HGI). The grazing angle fixed at $\sim 5^\circ$ permits to approximate the two configurations, respectively, to $\epsilon \parallel c$ and $\epsilon \perp c$, where $\epsilon$ is the polarization vector and $c$ is the wurtzite c-axis that corresponds to the sample surface normal. The number of acquired spectra and the integration time per energy point are chosen in order to obtain an edge jump of $\sim 10^4$ total counts per spectrum on each specimen. This permits to obtain the same statistics for all samples. The HERFD- and TFY-mode spectra are collected in the near-edge and extended regions (XANES and EXAFS) for the whole series.

Theoretical calculations are performed to support the analysis of the experimental XANES and EXAFS data. In order to simulate the Al$_x$Ga$_{1-x}$N:Mn series, five wurtzite supercells (SC), $3a \times 3b \times 2c$ (72 atoms), are built with the program VESTA [27], with Al concentrations of 0%, 25%, 50%, 75% and 100%, respectively. The experimental lattice parameters established from XRD measurements are employed for the SC, while the wurtzite $u$ parameter is chosen to be $u_{\text{GaN}} = 0.3869$ for Al up to 50% and $u_{\text{AlN}} = 0.3789$ for higher Al concentration (values from Ref. [28]). To simulate the Mn incorporation in the Al$_x$Ga$_{1-x}$N lattice the following defect configurations are taken into account: one Mn atom as 1) substitutional of Ga or Al (Mn$_u$); 2) interstitial in the tetrahedral (Mn$_{\text{T}}$) or octahedral (Mn$_{\text{O}}$) sites with Wyckoff positions, $\left(\frac{2}{3}, \frac{1}{3}, \frac{1}{2}\right)$ and (0, 0, $\frac{1}{2}$), respectively. This corresponds to a Mn concentration of $\sim$1%.

The lattice parameters and atomic positions of the SC are additionally relaxed by means of density functional theory (DFT) using the QUANTUM-ESPRESSO package [29]. The first-principles spin-polarized calculations are performed using a plane-wave basis and the projector augmented wave (PAW) method [30]. The exchange correlation energy is described by the Perdew-Burke-Ernzerhof parametrization within the generalized gradient approximation (PBE-GGA) [31]. The plane-waves cutoff energy is set at 60 Ry to ensure
convergence and the irreducible Brillouin zone is sampled with the Monkhorst-Pack scheme [32] using a 4×4×4 k-point mesh. For each Al concentration (x), the formation energies of Mn impurities substituting Ga or Al (Mn_{Ga,Al}) in Al_{x}Ga_{1−x}N (AlGaN) are calculated through E_{Mn} + E_{Ga,Al} = E[Mn_{Ga,Al}] + E[AlGaN] − E[AlGaN].

The Mn K-edge XANES and EXAFS spectra are simulated within the real-space Green’s function formalism by employing the FDMNES [33] and FEFF9 [34] codes. The muffin-tin potentials and the Hedin-Lunqvist approximation [35] for the exchange-correlation component are used. The calculations are performed using the DFT-relaxed SC rescaled FDMNES code [37], using a 4-point mesh. For each Al concentration (x), a second convolution with a Gaussian function of constant width (0.9 eV) is also applied to take into account the experimental broadening. For the EXAFS Debye-Waller factor, a constant value of 0.002 Å$^2$ is used to take into account the experimental broadening. The best agreement with the experimental data is found going from a Debye-Waller factor, a constant value of 0.002 Å$^2$ to a Debye-Waller factor, a constant value of 0.002 Å$^2$ at the maximum of the derivative peak corresponding to the typical shoulder after the pre-edge features.

RESULTS AND DISCUSSION

In this section the results of this study, based on XRD, (HR)TEM and XAS experimental techniques and supported by DFT-based simulations are presented and discussed. As a first step, we determine the Al content from the strain analysis on the XRD data. The XRD spectra of the symmetric (004) reflection over the whole series are reported in Fig. 1 (top panel). The Mn K-edge XANES and EXAFS spectral parameters account for the damping of the experimental EXAFS signal due to structural and thermal disorder. In both XANES and EXAFS simulations, the polarization effects [26] are correctly included. The EXAFS signal is extracted from the absorption spectra via the VIPER code [37], using a smoothing spline algorithm and selecting the edge energy $E_0$ at the maximum of the derivative peak corresponding to the typical shoulder after the pre-edge features.

FIG. 1. (Color online) XRD: (top panel) evolution of the GaN and Al$_x$Ga$_{1-x}$N (004) peak position over the whole series; (bottom panels) maps of the (T015) asymmetric reflection of GaN and Al$_x$Ga$_{1-x}$N measured for Al$_x$Ga$_{1-x}$N :Mn with 12% and 41% Al, respectively.

To gain insight into the Al content in the films, maps of the (T015) asymmetric reflection have been acquired for the whole series and are shown for the films containing 12% and 40% of Al, respectively (cf. Fig. 1 - bottom panels). The strain state of the Al$_x$Ga$_{1-x}$N layer is deduced from the relative position of the (T015) reflection of GaN and Al$_x$Ga$_{1-x}$N, and the a and c lattice parameters are obtained from the $Q_x$ and $Q_z$ coordinates of the Al$_x$Ga$_{1-x}$N (T015) reflection, upon a 2D Gaussian fit. To extract the Al concentration, we consider a linear variation of the lattice parameters between GaN and Al$_x$Ga$_{1-x}$N as a function of the Al concentration according to the Vegard’s law [38] for the relaxed structures. For the strained samples, the compressibility of Al$_x$Ga$_{1-x}$N through the Poisson coefficient is taken into account. The Al concentrations obtained from XRD – as summarized in Table I – are coherent within 1% error with those measured by EDS. The Al$_x$Ga$_{1-x}$N lattice parameters are reported in Fig. 2 and compared with those found with DFT calculations. The computed lattice parameters closely follow the Vegard’s law as in previous works based on full-potential augmented plane wave method calculations [39]. Moreover, the computed lattice parameters overestimate the experimental values by a mere ~1%.

We investigate via DFT also the formation energies for the incorporation of Mn in Al$_x$Ga$_{1-x}$N. For $x = 0.25$, 0.5, and 0.75, we compare the total energies for several structures with random position of Al and Ga atoms in cation positions. The total energies for each concentration do not differ...
by more than 50 meV. From this result, we conclude that the Al$_x$Ga$_{1-x}$N alloy has Al and Ga cations in random positions for all concentrations of the constituents. The second step is to investigate the formation energies upon the incorporation of Mn. We assume that for $x \leq 0.5$ Mn substitutes mostly Ga sites, whereas for $x > 0.5$ Mn ions replace Al sites. It is found that Mn$_{Ga}$ has a constant formation energy of 3.5 eV up to $x = 0.5$, while for Mn$_{Al}$ an abrupt increase in formation energy to 5.5 eV is obtained for $x > 0.5$. This result implies that, in terms of formation energy, Mn tends to substitute Ga atoms rather than Al ones, challenging the epitaxy to high-quality AlN:Mn. On the other hand, this does not take into account the surface energies that play a crucial role during the growth. Nevertheless, this result is confirmed by the experimental data, as reported in the following.

According to the TEM micrographs shown in Fig. 3, the layers are structurally homogeneous for Al concentrations up to 82%. Moreover, EDS spot sampling and line scans (not shown) confirm that the layers are chemically homogeneous as well. In contrast to the layer-by-layer growth of Al$_x$Ga$_{1-x}$N:Mn up to Al concentrations as high as 82% (Figs. 3a-d), the columnar structure of the AlN:Mn sample is evidenced in Fig. 3e. The Al$_x$Ga$_{1-x}$N:Mn layer with 82% Al is still structurally coherent with the GaN buffer layer, but at the boundary between 2D and 3D growth. The homogeneous structure of the Al$_x$Ga$_{1-x}$N:Mn layers with Al (a) 41%, (b) 59%, (c) 71% and (d) 82% is evidenced by the HRTEM images taken close to the [1120] zone axis and reported in Fig. 4. According to a Fast Fourier Transform (FFT) analysis, there is no compositional ordering or modulation of the Al concentration, in contrast to what was reported previously for Al$_x$Ga$_{1-x}$N layers without Mn [40]. In the HRTEM image of Fig. 4e the boundary between two columnar structures in the AlN:Mn layer is reported. Here, the arrow $a$ indicates a gap between the two columns, while arrow $b$ points to planar defects in the basal plane formed in the AlN:Mn layer.

Having established the lattice parameters (long-range structure), strain state and Al concentration with XRD, and the microstructure of the layers by means of TEM, we apply XAS to probe the local atomic and electronic structure around Mn impurities. The approach employed here follows a well-established method applied in previous studies of GaN:Mn [12, 41], GaN:Mn,Mg [42] and related systems as ZnO:Mn [43] and GaN:Sc [44]. Supported by the complementary spectroscopic techniques XANES, XLD and EXAFS, we demonstrate in the following that at least 90% of the Mn atoms incorporate into the Al$_x$Ga$_{1-x}$N lattice as random substitutional impurities at the cation site (Mn$_{A}$) in all the samples containing up to 82% of Al.

In Fig. 5 the normalized Ko1 HERFD-XANES spectra are shown together with their relative simulation for the HGI and VGI geometries. The HERFD-XANES spectra correspond to a diagonal cut in the two-dimensional resonant inelastic x-ray scattering (RIXS) plane [45] and can be approximated to a standard XANES spectra only in the region above the main absorption edge, where the spectral features arise from electric dipole transitions from 1s to 4p empty states of the absorbing atoms (Mn). This energy region can be described by multiple scattering theory within a one-electron approximation, i.e. the level of theory employed for the simulated spectra shown in this study. The spectral features present in the pre-edge region of the HERFD-XANES spectra cannot be fully described by such level of theory and line cuts in the RIXS planes [45]. For this reason, we do not take into account here the pre-edge ($1s2p$-RIXS) features and discuss only the fine structure above the absorption edge. The fine structure of the spectra and the trend with increasing Al concentration is reproduced by the simulations using a substitutional model as reported in Fig. 5. On the other hand, for such substantial changes in the crystal host (moving from GaN to AlN) it is not straightforward to quantitatively assign the evolution of the fine structure to a specific local environment change around the Mn atoms.

A more quantitative analysis to establish the percentage of Mn atoms incorporating as substitutional defects in the host matrix, is obtained by the analysis of the XLD spectra. It is es-
established that XLD is extremely sensitive to the symmetry of non-cubic sites [26] and it was shown to be a powerful tool to determine the quality of substutional inclusions in dilute magnetic semiconductors [46]. The XLD spectra for the studied samples are reported in Fig. 6 and are obtained from the difference between the HERFD-XANES spectra in VGI and HGI geometries. The amplitude of the XLD main oscillation at the edge position (highlighted region in Fig. 6) is taken as a figure of merit for Mn$_S$. In fact, the maximum XLD amplitude would be obtained for 100% Mn$_S$ dilute in a perfect Al$_x$Ga$_{1-x}$N lattice. As a reference for the 100% case, we arbitrarily rescale the experimental XLD amplitudes to the XLD amplitude at the Ga K-edge of a GaN:Mn layer from Ref. [47]. The results are reported in the inset to Fig. 6. The increasing values of the Mn$_S$ percentage for Al $\leq$ 82% are due to the accuracy of the normalization procedure employed. In fact, a more accurate procedure would require to rescale the Mn K-edge XLD amplitudes to the Ga K-edge (or Al K-edge) XLD amplitude measured for each sample in the same experimental conditions. On the other hand, the systematic errors are estimated to be within a $\pm$10% bandwidth. The dramatically low Mn$_S$ value for AlN:Mn can be safely attributed to an actual reduced Mn$_S$ content for this sample.

Having established via XLD that the majority of Mn atoms are incorporated as dilute Mn$_S$ in the host matrix, we further confirm this result based on the EXAFS analysis. This technique is a well established powerful tool for the local structure characterization of doped semiconductors [48, 49]. Here we follow a simulation approach in the EXAFS data analysis, i.e. we simulate the experimental spectra within a full mul-
multiple scattering expansion, without fitting parameters. This approach was shown to be valid on systems similar to those we consider [42, 44]. In addition, in our case the complexity of the system must be accounted for: not only the lattice is distorted locally by the introduction of the Mn$_S$ defects (similarly to e.g. GaN:Mn or AlN:Mn), but also the alloying effect due to the fact that we are dealing with the ternary compound Al$_x$Ga$_{1-x}$N plays a decisive role. By simulating ab initio the EXAFS spectra using the DFT-relaxed supercells rescaled to the experimental lattice parameters, it is possible to qualitatively validate the theoretical model (Mn$_S$) employed. A more quantitative analysis based on the standard Fourier transform analysis was not conclusive enough to be reported. In fact, the number of fitted parameters needed to model the system under investigation and the correlation between them do not permit to reach an agreement with the experimental data which is better than the one reached with the ab initio simulations.

In Fig. 7 the $k^2$-weighted EXAFS data are reported for the whole Al$_x$Ga$_{1-x}$N:Mn series. The full multiple scattering EXAFS simulations are over-imposed to the experimental spectra. The main phase and amplitude of the oscillations are reproduced, confirming the correct bond lengths and coordination numbers, respectively. The damping of the EXAFS signal (due to structural and thermal disorder) is also emulated, confirming the high crystalline quality of the films. Furthermore, the evolution of the spectra with increasing Al content is also reproduced as seen, for example, for the spectral features at $\approx 4$ Å$^{-1}$ and at $\approx 6$ Å$^{-1}$. This damping is understood by taking into account the destructive interference of the out-of-phase Mn-Ga and Mn-Al scattering paths in the cation-cation coordination shell. The agreement with HGI data is on the same level (not shown), further confirming that the Mn$_S$ is the most suitable model to describe the experimental data.

As final point we discuss the Mn valence state inferred from the integral of the absolute difference of the K$\beta$ XES data (integrated absolute difference – IAD analysis [45]). This method is preferred over the one employing the position of the main absorption edge for the possibility it gives to quantitatively follow the evolution of the effective spin moment on Mn ($S_{\text{eff}}$) as a function of a given parameter and to directly compare the results with DFT calculations [45]. The total magnetic moment per unit cell calculated with DFT is in all cases $4 \mu_B$ and corresponds to $S_{\text{eff}} \approx 2.0$, as found in the frame of a Bader partitioning scheme [45]. This result is confirmed experimentally, as reported in Fig. 8. The Mn valence state is constant within the error bar for the whole series, with the exception of the AlN:Mn sample, as expected and supporting all previous results.

**CONCLUSIONS AND OUTLOOK**

We have carried out an extensive study of epitaxial Al$_x$Ga$_{1-x}$N:Mn on a series of samples with Al concentration up to 100%. By XRD we have found that the Al content in the layers matches – over the sample series – the one
expected from growth conditions. The lattice parameters as a function of the Al concentration are compared and confirmed by DFT calculations. Furthermore, DFT computations on the formation energy for the incorporation of Al in a GaN matrix let us to conclude that Al and Ga are randomly distributed into the lattice, and in Al$_x$Ga$_{1-x}$N:Mn the Mn ions have the tendency to preferentially substitute for Ga in the lattice. A coherent growth without precipitation is obtained for Al$_x$Ga$_{1-x}$N:Mn with Al concentrations up to 82%, confirming the surfactant role of Mn already reported [21]. Synchrotron radiation XAS has been employed to probe the local atomic and electronic structure of Mn and the XLD analysis reveals that the majority of the Mn ions is dilute, i.e. homogeneously distributed over the doped layers, as further confirmed through EXAFS measurements. An IAD analysis of the XES data allows to determine the valence state of Mn as constant up to an Al concentration of 80%. Due to the reduced lattice parameters with respect to e.g. GaN:Mn, enhanced hybridization of the orbitals can be expected in Al$_x$Ga$_{1-x}$N:Mn, making it a material system worth to be investigated in view of spintronic functionalities. Moreover, this work paves the way to the understanding and control of the role played by Mn in particular and transition metals in general on the structure and properties of the alloys Al$_x$Ga$_{1-x}$N:TM. Significantly, the incorporation of Mn has been found to promote the growth of Al$_x$Ga$_{1-x}$N on GaN, to defer the relaxation of the layers and to increase the critical thickness also for Al concentrations up to 80%, with remarkable potential effects on the fabrication of e.g. distributed Bragg mirrors for III-nitride-based optoelectronic devices.

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**FIG. 8.** (Color online) Results of the IAD analysis over the whole series of samples. Inset: constant value of the spin magnetic moment over the whole range of Al concentrations, with the exception of 100%.
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