Direct evidence for implanted Fe on substitutional Ga sites in GaN

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The lattice location of iron in thin-film, single-crystalline hexagonal GaN was studied by means of the emission channeling technique. Following 60-keV room-temperature implantation of the precursor isotope ^{59}Mn at a dose of $1.0 \times 10^{13} \text{ cm}^{-2}$ and annealing up to 900°C , the angular distribution of β^- particles emitted by the radioactive isotope ^{59}Fe was measured by a position-sensitive electron detector. The β^- emission patterns around the [0001], [1102], [1101] and [2113] directions give direct evidence that the majority of Fe (80%) occupies substitutional Ga sites.

It is well known that iron on substitutional III sites in the cubic III-V semiconductors such as GaAs, GaP or InP acts as a deep acceptor [1]. The most prominent example with respect to applications is InP, where doping with Fe is used to produce semi-isolating material. Much less is known about Fe in the hexagonal III-V semiconductor GaN. Semi-isolating GaN would be useful, e.g., in high-temperature, high-power applications [2,3].

In an early investigation of the photoluminescence (PL) behavior of 35 elements implanted into GaN [4], merely damage-related luminescence around 2.15 eV was observed following the implantation of Fe ($5 \times 10^{18} \text{ cm}^{-3}$). However, this study only reported PL measurements in the energy range 1.5–3.6 eV. On the other hand, GaN layers grown by vapor phase epitaxy, which would normally be low-resistivity n -type, showed semi-isolating behavior if they contained high levels (up to $6.5 \times 10^{18} \text{ cm}^{-3}$) of Fe [5]. Considerably later [6] a sharp PL peak at 1.299 eV was discovered in the same samples used in the earlier studies of Ref. [5]. By means of optically detected magnetic resonance [6] this PL peak could be related to an electron spin resonance signal which exhibited the symmetry properties expected for Fe^{3+} on substitutional Ga sites in hexagonal GaN [6–8]. From PL excitation spectroscopy studies it was suggested that the deep acceptor level $\text{Fe}^{3+/2+}$ is located 2.5–2.6 eV above the valence band edge E_V [6,9,10]. However, more recent experiments have given evidence that this level lies much closer to the conduction band at $E_V + 3.17 \text{ eV}$ [11].

To date, Fe has been found to be a frequent contaminant in GaN thin films grown by metal organic vapor phase epitaxy (MOVPE), hydride vapor phase epitaxy (HVPE) [9,12], and by the sublimation sandwich method with typical Fe concentrations around 10^{17} – 10^{18} cm^{-3} [7,8]. On the other hand, attempts to intentionally produce Fe deep centers by doping during growth or by means of ion

implantation have not been very successful [3,13,14]. While GaN layers implanted with Fe up to 10^{19} cm^{-3} showed high sheet resistivity (10^9 – $10^{10} \Omega/\square$ in the as-implanted state and 10^{10} – $10^{12} \Omega/\square$ following moderate annealing), the resistivity decreased considerably upon annealing to 900°C [3,14]. Hence the semi-isolating properties must have been due to damage-related defects rather than electrically active deep Fe centers. The study of the lattice sites of implanted Fe may therefore help to clarify the processes, which hinder its electrical activation.

In this letter we report on the lattice location of ion implanted Fe in thin film, single-crystalline hexagonal GaN using the emission channeling technique [15]. The angular distribution of β^- particles emitted by the radioactive isotope ^{59}Fe ($t_{1/2} = 44.6 \text{ d}$) was monitored by a position-sensitive electron detector following room temperature implantation of the precursor isotope ^{59}Mn ($t_{1/2} = 4.6 \text{ s}$) at a dose of $1.0 \times 10^{13} \text{ cm}^{-2}$ and annealing up to 900°C . The sample was a commercially available GaN film of 1–2 μm thickness grown on sapphire. Implantations of 60 keV $^{59}\text{Mn}^+$ ions were performed at the ISOLDE on-line isotope separator facility at CERN. ISOLDE provides clean, mass-separated beams of radioactive Mn isotopes, which are produced by means of 1.4-GeV proton-induced nuclear fission from UC_2 targets and recently developed chemically selective laser ion sources [16]. During the β^- decay of ^{59}Mn (endpoint energies 4.4 MeV and 4.8 MeV) the ^{59}Fe atom receives a nuclear recoil around 200 eV, which assures that it is reimplanted and hence that its lattice position is not influenced by the previous site of ^{59}Mn . Emission channeling patterns from ^{59}Fe were extracted from the β^- energy window above 50 keV up to the endpoint energy of 461 keV. Corrections for electrons backscattered into the detector were implemented by subtracting a flat background from every pattern. We have quantified the backscattering contribution by means of simulations using the

FIG. 1. Angle-dependent β^- emission yields from ^{59}Fe in GaN around the [0001] (a), [1102] (b), [1101] (c) and [2113] (d) axes. The patterns were recorded following annealing at 200°C (c, d), 600°C (a) and 800°C (b). (e)-(h): best fits of simulated channeling patterns for S_{Ga} sites to the experimental yields.

EGS4 code [17], taking into account the elemental composition and geometrical features of the GaN film, the Al_2O_3 substrate, the Mo sample holder and the stainless steel vacuum chamber [18].

In order to identify the lattice sites of Fe, we have compared the experimental channeling yields to simulated patterns for ^{59}Fe emitter atoms on substitutional Ga sites S_{Ga} , substitutional N sites S_{N} , bond-centered sites both within and off the c -axis (abbreviated as BC- c and BC- o), anti-bonding sites AG- c , AN- c , AG- o and AN- o , the “hexagonal” sites HG and HN, and the so-called T and O sites. Note that the T and O sites are positions which are centered in the wide-open interstitial regions of the wurtzite lattice. Details on the simulation calculations, which were carried out using the “many beam” approach, as well as the location of the above-mentioned sites within the GaN lattice, can be found in Ref. [18].

Figure 1(a) [19] shows the [0001] β^- emission channeling pattern from the implanted GaN thin film following an annealing sequence up to 600°C. The channeling effects along the c axis and the major crystal planes are evidence that the majority of ^{59}Fe atoms occupy sites which are located within the c -axis atomic rows. The best two-fraction fit of the theoretical yields to the experimental data is shown in Fig. 1(e) and corresponds to 86% of Fe atoms along the c axis, and 14% on random (R) sites, which are

FIG. 2. Simulated channeling patterns for 100% of emitter atoms on HG sites [(a)-(d)] and O sites [(e)-(f)]. The orientation and angular resolution has been chosen so as to match the experimental patterns of Fig. 1. Note that the c axis patterns of HG sites (a) and O sites (e) are identical.

characterized by an isotropic emission yield. However, since S_{Ga} and S_{N} as well as AG- c , AN- c , BC- c and T sites are all located within the c axis, considering c -axis patterns alone does not provide unambiguous lattice site identification and additional crystal directions must be taken into account. Suitable directions in order to discriminate these sites are the [1102], [1101] and [2113] axes [18]. The emission channeling patterns of these three directions are shown in Figs. 1(b), (c) and (d). In all cases a combination of substitutional Ga sites and random sites provided the best two-fraction fit. Figures 1(f), (g) and (h) show the best fits to the [1102], [1101] and [2113] patterns, corresponding to 83%, 73% and 84% of Fe on S_{Ga} , respectively.

In order to illustrate that interstitial sites are responsible for emission patterns which are distinctively different from substitutional Ga sites, Figs. 2 (a-d) show the theoretical patterns for 100% of emitter atoms on HG sites, and Figs. 2 (e-h) for 100% on O sites. From a comparison of the simulated patterns with the experimental results of Figs. 1 (a-d) it is clear that large fractions of Fe on HG or O sites can be ruled out. However, fractions of 8(4)% of Fe atoms on HG (Ga-type “hexagonal”) or 5(3)% on O-type interstitial sites would be well in accordance with the experimental data, leading to an average improvement in the chi square of fit around 2.5(3)% and 1.0(3)% for all patterns. On the other hand, contributions from substitutional

FIG. 3. Fraction of Fe on substitutional Ga sites (a) and its room temperature rms displacements perpendicular to the indicated crystal directions (b) following isochronal (10 min) annealing steps. The dashed and dotted lines indicate the room temperature vibration amplitudes of Ga and N atoms.

N sites, which also exhibit characteristic channeling patterns [18], must be very small. Fits, where Fe on both S_{Ga} and S_N sites were allowed, resulted in fractions on S_N sites of less than 5% with insignificant improvements in the chi square of fit. Allowing for Fe on other interstitial sites such as H_N , BC or T, *etc* also did not significantly improve the quality of fit.

Annealing the sample at 200°C, 400°C, 600°C, 800°C and 900°C did not result in substantial changes in the fraction of Fe on S_{Ga} sites [Fig. 3 (a)]. This is the reason why in Fig. 1 we combined channeling patterns measured after different annealing temperatures but with best statistics. Figure 3 (b) shows the room-temperature root mean square (rms) displacements of Fe from the perfect substitutional Ga positions measured after the different annealing steps. As can be seen the rms Fe displacements, except perpendicular to the $[1101]$ direction, are clearly bigger than the vibration amplitudes of Ga and N atoms. This suggests that Fe is slightly displaced from the Ga sites in a specific crystal direction close to the $[1101]$ axis. With increasing annealing temperature, the rms displacements of Fe only show a slight tendency to decrease.

The maximum concentration of Fe in the peak of the implantation profile in our study, $6.5 \times 10^{18} \text{ cm}^{-3}$, is comparable to the value of 10^{19} cm^{-3} in Refs. [3,14]. Since our experiments show that around 80% of implanted Fe atoms are incorporated on substitutional Ga sites, the absence of deep Fe acceptors in the electrical measurements of Refs. [3,14] cannot be caused by Fe occupying non-substitutional lattice sites. We rather suggest that its electrical activation requires comparably high annealing temperatures (around 1100°C) as the activation of ion-implanted shallow *p*- or *n*-type dopants such as Mg, Ca or Si [2]. The reasons why such high annealing temperatures are required, might be complexes of the implanted atoms with lattice defects.

Summarizing, we have given direct evidence that Fe is mainly incorporated on substitutional Ga sites following room temperature ion implantation. Fractions of Fe on other lattice sites must be small, with the possible exception of HG or O sites. Annealing the implanted sample up to 900°C did not affect the substitutional Fe fraction. Ex-

cluding H, Li and Na, which partially occupied interstitial sites [20, 21], so far most implanted atoms (Si, Ca, Sr, In, Hf, and rare earths) were found to substitute for Ga atoms in GaN [18, 21-24]. In that respect, implanted Fe forms no exception. Lattice location results for possible N-site impurities such as O, P or As, however, have not been reported so far.

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