EMISSION CHANNELING EXPERIMENTS FROM THE DECAY OF ^{149}Gd TO ^{149}Eu IN GaN

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Abstract

The lattice site location of excited states of ^{149}Eu was studied by means of the emission channeling technique. 60 keV implantation of ^{149}Tb into a GaN thin film was performed at room temperature up to a dose of $2.0 \times 10^{13} \text{ cm}^{-2}$. This radioactive isotope eventually decays into short-lived excited states of ^{149}Eu . The conversion electrons emitted in the subsequent decay to the ^{149}Eu ground state were detected with a position sensitive detector. We measured their angular distributions around the [0001], [1102], [1101] and [2113] axes in the as-implanted state and after 600°C and 900°C vacuum annealing. Already in the as-implanted state around 65% of ^{149}Eu atoms were found on substitutional Ga sites. The root mean square (rms) displacements from the substitutional sites in the as-implanted state were found to be around 0.13-0.16 Å. Annealing up to 600°C increased the substitutional fraction by a few percent and slightly reduced the rms displacements, most likely due to the removal of crystal defects in the vicinity of the Eu atoms, resulting in a better incorporation into substitutional sites.

Keywords: Lattice location, Emission channeling, GaN, Europium, Ion implantation

1. Introduction

GaN is a widely used host material for fabricating bright optoelectronic devices such as LEDs, operating in the infrared to ultraviolet region of the spectrum. Most of the attention so far has gone to GaN and its related alloys InGaN and AlGaN whose composition was tuned to achieve the suitable band gap for the desired emission wavelength.

A promising alternative method of manufacturing luminescent devices is rare earth doping of GaN [1,2]. This approach is based on the emission of photons produced by intra-4f shell transitions of excited rare earth atoms. The advantage is that no alloying is required and that the corresponding electroluminescence from such devices is temperature-stable and has a narrow line width. Successful operation of RE doped electroluminescent devices has already been obtained by Tm [3,4] (blue), Er [3,5] (green and infrared), Pr [6] (red or infrared) or Eu [3,7] (red) doping of GaN. The rare earths species were introduced into the GaN crystal either during growth or by ion implantation. The latter has the additional advantage that the lateral and depth profile of the dopant species can be accurately controlled, but has the drawback that defects are introduced in the crystal.

Since the crystal field affects the splitting and intensity of optical transitions between the 4f levels, understanding the lattice site location and atomic surroundings of the RE atoms is essential. A previous Rutherford backscattering spectroscopy/channeling (RBS/C) study [8] suggested Eu^{3+} to be on a site that is displaced by 0.2 Å along the [0001] axis with respect to a substitutional Ga site. Another work [9] based on extended X-ray absorption fine structure (EXAFS) experiments showed evidence of two kinds of bond lengths between Eu and N, which is compatible with the model of Eu^{3+} on a Ga displaced site. No reference could be found to the use of Gd as a dopant in GaN.

In this article the lattice location of ^{149}Eu in GaN was investigated by means of the emission channeling technique [10,11]. This technique makes use of the fact that charged particles that are emitted in the decay of radioactive nuclei experience channeling or blocking effects along the major axes and planes of the host crystal. The resulting anisotropic emission yields depend characteristically on the lattice sites occupied by the radioactive isotopes.

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2. Experimental

The hexagonal, single-crystalline GaN layer was grown on a sapphire substrate by metalorganic chemical vapor deposition (MOCVD). 60 keV implantation of ^{149}Tb ions was performed at the ISOLDE facility at CERN. We implanted the sample using a 1 mm diam. beam spot to a dose of $2.0 \times 10^{13} \text{ cm}^{-2}$ at an angle of 7° from the surface normal to avoid channeling.

Because of their similar mass and the construction of the ion source the ion beam not only contained ^{149}Tb but also some ^{133}CeO contamination. By storing the sample for 4 days after implantation, most of the ^{149}Tb ($t_{1/2} = 4.15 \text{ h}$) has decayed to ^{149}Gd through electron capture (83%) and into ^{145}Eu through α decay (17%). By then the contaminant ^{133}Ce has decayed to the long-lived isotope ^{133}Ba ($t_{1/2} = 10.5 \text{ y}$) that doesn't interfere with our experiment. Also the decay chain of ^{145}Eu doesn't affect our measurements.

Fig. 1. Simplified decay scheme of ^{149}Gd to ^{149}Eu . Only the relevant high intensity transitions are shown. f_K , f_L and f_M are conversion electron intensities with reference to the decay of ^{149}Gd for emission of respectively K, L and M electrons by the excited states of ^{149}Eu .

After the decay of ^{149}Tb the ^{149}Gd nucleus receives a recoil energy of 48 eV. Although no values of displacement energies of Ga or N atoms in GaN could be found in literature, they should be somewhere between the values for Si (21 eV) [12] and diamond (40 eV) [13]. This means that the recoil energy is probably sufficient to reimplant the ^{149}Gd nucleus so that its lattice site is independent of the lattice site it occupied before the decay. This isotope then decays ($t_{1/2} = 9.3 \text{ d}$) mainly into short-lived excited states of ^{149}Eu . In the subsequent decay cascade to the ground state there are 3 transitions in which conversion electrons are emitted (Fig. 1). These conversion electrons were used in our emission channeling experiment. Because they are emitted by the excited states of ^{149}Eu , the experiment will give direct information on the lattice location of the Eu atom during the time window of a few ns to μs while its nucleus was in the excited states resulting from the ^{149}Gd decay. Note, however, that the recoil energy of the ^{149}Gd decay is only of the order of 0.5 eV to 5 eV. Most probably the excited Eu nuclei will thus inherit the lattice site of ^{149}Gd .

Using a two-dimensional position-sensitive Si detector the angular distributions of the conversion electrons were measured around the [0001], [1102], [1101] and [2113] crystal axes. Such a set of patterns was recorded for the as-implanted state and after 10 min isochronal vacuum annealing at 600 and 900°C.

One of the problems in electron emission channeling experiments is the backscattering of electrons by the sample and by components of the vacuum setup. These electrons give rise to an isotropic background in the angular emission patterns. In order to quantify this background Monte-Carlo simulations based on the GEANT4 code [14] were used. The code took into account the composition and geometry of the GaN sample, the sapphire substrate, the Mo sample holder and the stainless steel vacuum chamber walls.

In order to analyze the experimental emission channeling patterns theoretical patterns were calculated for the emitting isotope on different lattice sites within the GaN crystal. These calculations used the 'many beam' approach for electron channeling in single crystals. The experimental data were fitted to the theoretical emission yields using a two-dimensional fitting procedure [11]. Besides Eu on substitutional Ga (S_{Ga}) or N (S_{N}) sites with various vibration amplitudes we also considered interstitial sites: bond-centered and anti-bonding sites within and off the c -axis, the 'hexagonal' sites HG and HN and the so-called T and O sites [15], as well as various displacements between these sites.

3. Results and Discussion

Figure 2(a) shows the anisotropic emission pattern measured along the [0001] direction after 10 min vacuum annealing at 900°C. The channeling effect along the c -axis and the intersecting planes suggests that ^{149}Eu is situated along the atomic rows in this direction. This does not, however, prove the substitutionality of ^{149}Eu , since there are also several interstitial sites along the c -axis. The best two-fraction fit of theoretical patterns to the experimental data (Fig. 2(e)) corresponds to a fraction of 66% of ^{149}Eu atoms located along the c -axis. The remainder is situated on random (R) sites which give an isotropic contribution to the emission yield. Probably these are ^{149}Eu atoms located on a mixture of several low-symmetry sites or sites with disordered surroundings. The analysis also showed the one-dimensionally projected root mean square (rms) displacement perpendicular to [0001] rows u_1 to be 0.12 Å. Additional emission patterns were measured along the [1102], [1101] and [2113] axes in order to discriminate between the different sites located along the c -axis (Figs. 2(b)-(d)). The analysis of

Fig. 2. (a)-(d) Angle-dependent emission yields of conversion electrons from ^{149}Eu in GaN after 10 min vacuum annealing at 900°C . The channeling patterns were extracted for an energy window above 88 keV, corresponding to the highest intensity conversion electron lines coming from ^{149}Eu . (e)-(h) Best fits of simulated channeling patterns for S_{Ga} sites to the experimental yields, corresponding to 66%, 66%, 57% and 69% of Eu on S_{Ga} sites and rms displacements of 0.12 Å, 0.14 Å, 0.10 Å and 0.11 Å respectively.

Fig. 3. Simulated channeling patterns for 100% of emitter atoms located on S_{N} sites (a)-(d) and O sites (e)-(h). Note that the c -axis channeling patterns for S_{N} sites (a) are identical to those of S_{Ga} sites (Fig. 2(e)), because they lie along the same c -axis row.

these data showed 66%, 57% and 69% of Eu atoms on substitutional Ga sites (S_{Ga}) with rms displacements of 0.14 Å, 0.10 Å and 0.11 Å, respectively. In order to show that different sites correspond to distinctively different emission patterns, Figures 3(a)-(d) show the theoretical yields for 100% of emitter atoms on substitutional N sites (S_{N}) and Figures 3(e)-(h) for 100% on interstitial O sites. Allowing such additional lattice sites in the fits did not significantly improve the chi square. However, small fractions (< 7%) of ^{149}Eu on S_{N} , HG or O sites would still be in accordance with the experimental data.

Figure 4(a) displays the fraction of ^{149}Eu atoms on S_{Ga} sites as a function of annealing temperature. These are the averages of the four directions that were investigated following each annealing step. The error bars are the corresponding standard deviations. Already in the as-implanted state a high fraction (65%) of ^{149}Eu atoms is located on S_{Ga} sites. No significant improvement could be observed after annealing.

The influence of annealing on the rms displacements is shown in Figure 4(b). In the as-implanted state the displacements are larger than the thermal vibration amplitude of Ga in GaN, which is 0.074 Å [16]. This suggests that the ^{149}Eu atoms are slightly displaced from the Ga sites, probably due to point defects in the vicinity. Also note that these displacements differ for the 4 crystal axes, which would point to preferential displacement directions in the crystal. After annealing to 600°C the rms displacements decrease significantly, most likely due to a partial removal of the surrounding defects, which leads to a better incorporation into the Ga substitutional site.

Fig. 4. The fraction (a) of ^{149}Sm atoms on substitutional Ga sites and the corresponding 1-dimensionally projected root mean square displacements u_1 perpendicular to the indicated crystal directions (b) as a function of annealing temperature.

These observations qualitatively match the results of our previous emission channeling work on other rare earth species in GaN. Also for ^{143}Pr [17], ^{147}Nd and ^{147}Pm [18] we found high fractions of RE atoms (up to 80%) on substitutional Ga sites which didn't change after annealing. The rms displacements were also found to be anisotropic and even larger than in the case of ^{149}Sm .

These findings are however in contrast to the results obtained earlier by RBS/C and EXAFS, which suggest a site that is displaced from the S_{Ga} site along the c -axis by 0.2 Å. The emission channeling technique is able to detect displacements much smaller than this. One possible explanation for this discrepancy is that in our case we are probing ^{149}Sm Eu lattice sites which are occupied as a result of the ^{149}Gd decay and its nuclear recoil, and are therefore somewhat different from the equilibrium Eu positions. Another possibility is, that the 1000°C anneal step, to which the GaN:Eu sample was subjected prior to the RBS measurements of Ref [8], resulted in a different damage annealing and change of the local structure.

4. Conclusions

Summarizing, our experiments gave direct evidence that the majority of ^{149}Sm Eu atoms prefer a substitutional Ga site in GaN. Already after room temperature implantation we found a substitutional fraction of around 65%. Annealing up to 900°C did not significantly improve this fraction. However, the rms displacements did decrease, which we attribute to the removal of crystal defect in the vicinity of the RE atom.

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