Implantation Studies on Silicon-Doped GaN

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Silicon-doped GaN layers grown by low-pressure metalorganic vapor-phase epitaxy with Si concentrations ranging from 2×10^{17} Si/cm³ to 9.2×10^{18} Si/cm³ were investigated by means of the perturbed angular correlation (PAC) technique applied to implanted ¹¹¹In(Cd). An undoped GaN film is used as a reference. The Si atoms replace Ga atoms in the lattice, and silicon, being a group IV element, acts as a donor on the Ga site and contributes one extra electron to the conduction band. Hall-effect measurements confirmed that the free charge carrier density is essentially increased and of the order of the silicon concentration. PAC investigations of the annealing behavior after implantation of the ¹¹¹In probes show that best recovery is achieved after annealing at 1200 K and that high silicon concentrations make GaN films more stable at high temperatures. Further, it was found that the temperature dependence of the electric field gradient is reduced by increasing Si concentrations.

Key words: Nitride semiconductor, implantation, annealing, perturbed angular correlation

INTRODUCTION

Group III nitride semiconductors, especially gallium nitride (GaN), have drawn much attention in recent years. One remarkable feature of these materials is the formation of continuous alloy systems, e.g., In_xGa_{1-x}N, in which the optical bandgap can be tailored by varying the concentrations of the constituents. This makes group III nitrides ideal for optoelectronic devices. In order to improve the possibilities of structuring GaN devices it is desirable to dope the material by ion implantation. Then, however, lattice damage is created and has to be annealed by an appropriate temperature program. Thus, in this work the effect of doping on the annealing behavior after ion implantation and stability of GaN films at high temperatures is investigated. Further, the influence of changes in the charge carrier density on the hyperfine fields in GaN and their temperature dependence is studied. A nuclear technique, namely the perturbed angular correlation technique, is employed in this work.

EXPERIMENTAL PROCEDURES

The perturbed angular correlation (PAC) method is an experimental technique of nuclear solid-state physics. It is based on the hyperfine interaction between a radioactive probe atom and fields present at the position of the probe atom. In more detail, the nuclear electric quadrupole and magnetic dipole moment interact with electric field gradients (EFG) and magnetic fields, respectively. In solids, an EFG can originate from the charge distribution in a noncubic crystal lattice such as the wurtzite structure found in many group III nitride semiconductors. Crystal defects such as substitutional and interstitial impurities or vacancies also lead to an EFG. Thus, lattice damage, which unavoidably occurs during the doping of semiconductors by ion implantation, can be investigated in detail by PAC.

Experimentally, the hyperfine interaction is observed in the time-dependent change of the angular correlation between two successive γ -rays in a γ - γ cascade due to an external perturbation by an EFG. A comprehensive description of the theory of perturbed angular correlation can be found in the literature.¹

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Table I. Silicon concentration and thickness of the doped layer measured with SIMS

Sample Number	Si Concentration (atoms/cm ³)	Layer Thickness (nm)
GN 5465	Undoped	2,400
GN 5499	2.0×10^{17}	890
GN 5895	6.0×10^{17}	980
GN 4877	1.1×10^{18}	900
GN 4876	3.7×10^{18}	900
GN 4885	9.2×10^{18}	970

In the present experiment, the angular correlation of the 172 keV–245 keV γ – γ cascade emitted in the decay of the PAC probe ^{111}In to ^{111}Cd was measured in conventional fast–slow PAC setups equipped with BaF_2 or lutetium oxyorthosilicate (LSO) scintillators coupled to fast photomultipliers. Further details on these two systems can be found in the PhD theses of Koch² and Valentini.³ From the data, the quadrupole interaction (QI) frequency $\nu = eQV_{zz}/h$ as well as the symmetry of the EFG (η) and its orientation can be derived. Any damping of the QI frequency gives information on remaining defects near the probe atoms. The fraction of

Fig. 1. Time-dependent anisotropy $A_{22}(t)$ for ^{111}In after implantation into GaN samples with different Si doping levels (undoped: left side; 9.2×10^{18} Si/cm³ doped: right side). The c -axis of the crystal is aligned at an angle of 45° relative to the start detector in the detector plane. Top to bottom: spectra obtained after annealing for 120 s under nitrogen at the temperature indicated in the frames.

Fig. 2. (a) Fractions of In probe atoms in GaN on regular lattice sites after annealing at different temperatures and (b) the width of the frequency distribution around the lattice QI frequency (open squares = highest Si doping of $9.2 \times 10^{18}/\text{cm}^3$; open circles = undoped).

implanted atoms in the same environment is directly proportional to the amplitude of the respective QI pattern in the $A_{22}(t)$ spectra.

SAMPLE PREPARATION

All samples investigated in this study were grown by metalorganic vapor-phase epitaxy (MOVPE) on 2-inch sapphire substrates in *c*-direction, Ga face. The layer sequence consists of a 25-nm GaN low-temperature nucleation layer followed by an undoped 2- μm GaN buffer layer, in order to improve the crystal quality. On top of that, silicon-doped GaN layers with different thicknesses ranging from 890 nm to 970 nm were grown. For this study, silicon-doped GaN films with five different concentrations ranging from $2 \times 10^{17} \text{ Si}/\text{cm}^3$ to $9.2 \times 10^{18} \text{ Si}/\text{cm}^3$ were available. Additionally, an undoped GaN film (GN 5465) of 2.4 μm thickness is used as a reference. The silicon concentration and thickness of the doped layer were measured using secondary-ion mass spectrometry (SIMS). Further details about the sample properties can be found in Table I and in an article of Köhler et al.⁴

Implantation of ^{111}In PAC probe atoms was carried out at the Bonn Isotope Separator. To prevent channeling of the implanted ions, the samples were tilted by an angle of 7° with respect to the ion beam

direction. According to previous studies in our group, no channeling effects are to be expected in this configuration. The implantation energy was set to 160 keV, and a typical dose of $1 \times 10^{12} \text{ In}/\text{cm}^2$ was reached. The mean implantation depth is simulated to be 399 Å, the full-width at half-maximum (FWHM) of the implantation profile to be 158 Å, and the maximum implantation depth to be 1163 Å.⁵ Comparing the maximum implantation depth with the thickness of the doped layers (Table I), it is obvious that the indium probes do not reach the GaN buffer layer beneath the silicon-doped layer.

Annealing steps were carried out under nitrogen atmosphere between carbon strips in a rapid thermal annealing setup. To exclude variations in the annealing conditions, normally two samples were annealed together face to face, thus serving as a proximity cap to each other. For measurements at elevated sample temperatures a PAC furnace was used.⁶

MEASUREMENTS AND RESULTS

After implantation, the crystal lattice is heavily damaged, as expected, and most of the probe atoms are not located at substitutional sites. Thus, each probe atom is subjected to a different EFG. These EFGs strongly differ in magnitude and orientation in space, causing a quick breakdown of the anisotropy within the first 20 ns of the time window (Fig. 1, top row) independent of the Si concentration.

The recovery of the crystal lattice from the implantation-induced damage was monitored by taking PAC spectra at 293 K after annealing the samples for 120 s at several temperatures from 600 K up to 1400 K. Distinct differences depending on the Si concentration could be observed. This can be seen most clearly in Fig. 2, where the spectra obtained from the undoped sample and the one with the highest Si concentration are compared. The unique QI $\nu_Q \approx 6 \text{ MHz}$ expected for In on a Ga site in GaN⁷ develops more clearly in the highly doped sample (annealing temperatures above 600 K in Fig. 2) and reaches its maximum after annealing at 1200 K (Fig. 2 top). Here, a least-squares fit to the data yields a fraction of 87(1)% of the probe atoms on the regular lattice site as compared with 62(1)% for the undoped sample. Even after the 1400 K step, the highly doped sample still shows 44(1)% of In on this site, whereas in the undoped sample the QI has disappeared completely and instead a largely undisturbed spectrum is found. The undisturbed spectrum is a well-known phenomenon which occurs when nitrogen is completely lost from the top crystal layers and the In probe atoms are dissolved in the remaining liquid Ga drops.⁸ The different behavior of Si-doped and undoped sample was verified by taking pictures of the sample surface by optical microscopy, where larger and more numerous Ga droplets were found on the undoped sample. A possible explanation for this effect might be the

Fig. 3. Parameters derived from a least-squares fit to $A_{22}(t)$ spectra taken at elevated sample temperatures for the substitutional and defect-associated site. Lines are inserted to guide the eye.

formation of strong Si–N bonds as in silicon nitride, which prevent nitrogen from diffusing out of the sample with high Si content.

Measurements with different sample orientations confirmed that in all samples the principal component of the EFG is axially symmetric ($\eta = 0$) and parallel to the c -axis of the crystal as observed in previous studies.⁷

At room temperature, after annealing at 1200 K, the EFG increases with the silicon concentration (Fig. 3). This can be due to a change of the u parameter, caused by the incorporation of silicon atoms, or an increase of the charge carrier density.⁹

Temperature-dependent measurements up to 900 K showed that the increase of the EFG with temperature is less pronounced when doping with concentrations larger than 3.7×10^{18} Si/cm 3 .

Furthermore, compared with undoped GaN, lower damping of the QI frequency is observed up to a concentration of 1.1×10^{18} Si/cm 3 at room temperature. These results can be attributed to a reduced dislocation density, caused by the silicon doping.¹⁰ This reduction of the damping is enhanced at higher temperatures. At 900 K, up to 3.7×10^{18} Si/cm 3 , lower damping than for undoped GaN is measured.

In all samples, a minor fraction of probe atoms subjected to a much larger EFG is observed in the PAC spectra. This fraction is attributed to a nitrogen vacancy, trapped by the oversized In probe atoms on the nearest N site in c -direction.^{11,12} At room temperature, this fraction decreases with the silicon concentration. Since in recent density functional calculations by Ganchenkova and Nieminen¹³ it was found that in n -type GaN negatively charged

nitrogen vacancies are the dominating defect, it is most probable that ionized donors, in this case Si^+ , act as competing traps for N vacancies.

CONCLUSIONS

The annealing behavior of Si-doped GaN was studied after implantation of various doses of In. By means of the perturbed angular correlation technique applied to the nuclear probe ^{111}In it could be shown that the optimum annealing condition was 1200 K for 120 s under nitrogen atmosphere. Large Si concentrations in the implanted GaN films were found to effectively stabilize the GaN surface at high annealing temperatures.

REFERENCES

1. H. Frauenfelder and R.M. Steffen, *Alpha, Beta, and Gamma-Ray Spectroscopy*, ed. K. Siegbahn (Amsterdam, The Netherlands: North-Holland, 1965).
2. H. Koch, *Defekt-Fremdatom Wechselwirkung in den hexagonalen Metallen Rhenium und Lutetium* (PhD thesis, Universität Bonn, 1992).
3. R. Valentini, *Winkelkorrelationsuntersuchungen an Seltenen Erden in Halbleiter mit großer Bandlücke* (PhD thesis, Universität Bonn, 2011).
4. K. Köhler, J. Wiegert, H.P. Menner, M. Maier, and L. Kirste, *J. Appl. Phys.* 103, 023706 (2008).
5. J.F. Ziegler, J.P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Solids* (New York: Pergamon, 1985).
6. M. Forker, W. Herz, U. Hütten, R. Müßeler, J. Schmidberger, D. Simon, A. Weingarten, and S.C. Bedi, *Nuclear Instrum. Methods A327*, 456 (1993).
7. K. Lorenz, F. Ruske, and R. Vianden, *Appl. Phys. Lett.* 80, 4531 (2002).
8. G. Marx, *Akzeptor-Wasserstoff-Komplexe und spannungsinduzierte elektrische Feldgradienten in Silizium und Germanium* (PhD thesis, Universität Bonn, 1995).
9. M. Corti, A. Gabetta, M. Fanciulli, A. Svane, and N.E. Christensen, *Phys. Rev. B* 67, 064416 (2003).
10. S. Ruvimov, Z. Liliental-Weber, T. Suski, J.W. Ager III, J. Washburn, J. Krueger, C. Kisielowski, E.R. Weber, H. Amano, and I. Akasaki, *Appl. Phys. Lett.* 69, 990 (1996).
11. P. Pyykkö, *Phys. Rev. B* 85, 24115 (2012).
12. P. Keßler, K. Lorenz, and R. Vianden, *Defect Diffusion Forum* 311, 167 (2011).
13. M.G. Ganchenkova and R.M. Nieminen, *Phys. Rev. Lett.* 96, 196402 (2006).