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Paramagnetic defects in GaN

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In this work, paramagnetic defects in wurtzite GaN crystals were systematically studied using the Electron Spin Resonance (ESR) technique and using electrical measurements. Three different resonance signals were found. The first had $g_{||} = 1.9514 \pm 0.0005$ and $g_{\perp} = 1.9486 \pm 0.0005$, a commonly observed defect in n-type crystals ascribed to the shallow donor of GaN [1]. The second ESR signal, an anisotropic line of $g_{||} = 2.0728 \pm 0.0015$ and $g_{\perp} = 1.9886 \pm 0.0015$, was observed only in Mg-doped p-type GaN layers, and was assigned to the Mg acceptor. The last ESR resonance signal, an isotropic line with $g = 2.0026 \pm 0.0005$ was observed only in AMMONO GaN crystals after thermal annealing, as well as in Mg-doped GaN epitaxial layers. It was tentatively identified as due to a deep acceptor.

1 Introduction

The Electron Spin Resonance (ESR) method is a useful tool for identification of defects and impurities in crystal structure. These defects and impurities usually introduce both shallow and deep states in the gap region, and play an important role for electrical and optical properties of semiconductors. Application of gallium nitride (GaN) for blue to near ultraviolet light emitting devices and high-temperature electronics [2] requires an understanding of the nature and properties of both intrinsic and extrinsic defects, and also requires a control of crystal doping. Therefore, we applied the ESR technique for defect studies of GaN crystals grown by different methods.

Undoped GaN crystals are typically n-type conductive with carrier concentrations between 10^{16} and 10^{19} cm^{-3}. However, the nature of the residual donor has not been positively identified and N vacancies [3] [4], oxygen [5] and silicon [6] have been proposed as possible candidates. Indeed, silicon has been commonly used as the intentional donor dopant up to the 10^{20} cm^{-3} concentration range [7], although typical gallium-rich growth conditions of GaN cannot exclude the presence of nitrogen vacancies. Oxygen contamination is also difficult to avoid. As for p-type GaN, magnesium is the only acceptor in GaN crystals so far that can be used to obtain useful p–type conductivity in a reproducible way. However, in as-grown Mg doped crystals obtained by metal organic chemical vapor deposition (MOCVD), a passivation process plays a crucial role in the compensation mechanism causing creation of neutral magnesium–hydrogen complexes [8]. Therefore, a post-growth treatment is required to activate the Mg acceptors [9]. Mg-doped GaN epitaxial layers obtained by molecular beam epitaxy (MBE) method are p-type without any post-growth treatment [10] because this technique does not involve hydrogen during growth.

In this work, paramagnetic defects in GaN crystals were systematically studied using ESR technique and electrical measurements. Our results revealed the presence of three different resonance signals, which are described successively below.

2 Experiment

The investigated GaN heteroepitaxial layers were grown on sapphire substrates by the horizontal MOCVD technique using an adapted Epigress system in the Crystal Growth Laboratory of Warsaw University. The growth was initiated with a deposition of a low temperature GaN buffer layer and was performed at temperatures close to 1000°C. The layers had pure wurtzite structure [11].

The GaN layers were: intentionally undoped, with electron concentration n in the range of $3\cdot10^{16}$ cm^{-3} to $5\cdot10^{17}$ cm^{-3}; Si-doped, with n in the range of $2\cdot10^{17}$ cm^{-3} to $7\cdot10^{18}$ cm^{-3} ; and Mg-doped, highly resistive directly after their growth process and with hole concentration of about $8 \cdot 10^{17}$ cm^{-3} after rapid thermal annealing (RTA) at temperatures 750°C for 10 minutes in an N_2 atmosphere.

The investigated AMMONO GaN crystals were in the form of crystalline powder. The AMMONO method applied for GaN growth has been described elsewhere [12], and it consisted of gallium nitridization in supercritical ammonia (at temperatures up to 500°C and pressure in the range of 4 to 5 kbar). Some of the crystals were grown in the presence of erbium.

Some of the GaN crystals were thermally annealed in a furnace at temperatures in the range of 100°C to 750°C for about 5 minutes in air or ammonia atmosphere and in the MOCVD in a molecular H_2 atmosphere at 550°C for half an hour.

ESR experiments were carried out using a Bruker ESP–300 X-band spectrometer operating at a microwave frequency of about 9.4 GHz. A helium gas-flow Oxford Instruments cryostat was used for variable temperature operation between 4 and 300 K. The values of g-factor were estimated by comparison with a standard Si:P sample.

The van der Pauw method was used for electrical transport measurements. GaN samples were mounted in a close cycle refrigerator with a possibility of temperature change between 13 to 400 K and placed in a magnetic field of about 250 mT. For n-type layers, ohmic contacts were prepared using metallic indium, whereas for p-type layers, evaporation of nickel and gold with subsequent annealing at 500°C for 30 s was applied.

3 Results and discussion

Undoped as well as Si-doped MOCVD epilayers were n-type conductive, and for samples with electron concentrations up to 10^{18} cm^{-3} ESR, an anisotropic line with $g_{||} = 1.9514 \pm 0.0005$ and $g_{\perp} = 1.9486 \pm 0.0005$ was observed. The anisotropy and the g-factor value were the same as for the line observed for undoped wurtzite GaN films by Carlos et al. and attributed to native shallow donor centers [1]. Therefore we identified the line observed for undoped and Si doped MOCVD layers as that due to shallow donors. The intensity of the line increased with increase of Si dopant up to 10^{18} cm^{-3}. Above this concentration the line broadened and was undetectable for $n = 6 \cdot 10^{18}$ cm^{-3}. We also detected an ESR resonance with similar parameters for AMMONO GaN crystals grown in the presence of Er. However, the ESR line showed no anisotropy in this case, because the measurement was performed on powdered material. The line was identified as an average signal of the anisotropic donor line seen by Carlos et al. [1]. The similarity of the ESR line exhibited by native as well as Si donors in GaN suggested a dominant influence of crystal band structure on the g-factor.

As-grown Mg-doped epilayers were of high resistivity because of the known effect of acceptor passivation by hydrogen [8] [9]. Prior to annealing, they did not show any paramagnetic signal. RTA of Mg-doped crystals led to hydrogen outdiffusion and as a result to p-type conductivity of the layers. Also, a new anisotropic ESR signal with $g_{||} = 2.0728 \pm 0.0015$ and $g_{\perp} = 1.9886 \pm 0.0015$ was found. We assign this resonance signal to the magnesium acceptor in the neutral charge-state. A resonance signal of similar parameters has been observed by optically detected magnetic resonance (ODMR) technique and ascribed to Mg acceptor as well [13] [14].

Introduction of hydrogen into GaN:Mg films by thermal annealing in ammonia atmosphere caused a decrease of the ESR line related to Mg acceptors and led to its complete disappearance after 30 minutes of annealing at temperature 600°C. Another RTA annealing in an N_2 atmosphere restored the Mg-acceptor line. The observed changes in the magnesium related ESR signal are shown in Figure 1. The annealing of some GaN crystals in the temperature range of 300°C to 750°C resulted in the appearance of a new isotropic ESR signal with g-factor equal 2.0026 ± 0.0005.

In the case of AMMONO GaN crystals, it was necessary to perform the annealing in air. Under such conditions the isotropic ESR line intensity increased with increasing annealing temperature up to about 500°C (see Figure 2). The signal intensity decreased to zero after thermal annealing at temperature about 700°C. This signal could be restored repeatably by lower temperature annealing, but only when the annealing was performed in air.

The same ESR signal, an isotropic line with $g = 2.0026 \pm 0.0005$, has been observed in Mg-doped GaN MOCVD epilayers after thermal annealing in molecular hydrogen (H_2) at 550°C. This kind of thermal annealing did not result in hydrogen passivation of defect centers in GaN crystals, because after the annealing, the Mg-acceptor ESR line was still present. Just as for AMMONO GaN crystals, thermal annealing of MOCVD GaN:Mg at 700°C in air caused a disappearance of the isotropic resonance line. For now, it is difficult to identify the ESR line. However, since the temperature region in which the line is created and annihilated is similar to that of hydrogen diffusion in GaN crystals, we tentatively ascribe it to a deep acceptor that can be passivated by hydrogen.

In summary, ESR measurements of n-type GaN crystals showed a similarity of resonance lines exhibited by both native and Si-donors, which suggested that the crystal band structure has dominant influence on the g-factor. A new anisotropic signal of the magnesium acceptor in a neutral charge-state was measured in the ESR spectra of Mg-doped GaN epilayers. A passivation process of Mg-acceptors resulting from thermal annealing could be observed by tracing changes in the Mg-acceptor ESR line. The creation of a new paramagnetic deep defect by thermal annealing in the range of 300°C to 750°C was observed in AMMONO GaN crystals as well as in GaN:Mg epilayers.

ACKNOWLEDGMENTS

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REFERENCES

[1] W. E. Carlos , J. A. Freitas, Jr., M. Asif Khan, D. T. Olson, J. N. Kuznia , *Phys. Rev. B* ***48*** , 17878-17884 (1993).

[2] H. Morkoc, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, M. Burns , *J. Appl. Phys.* ***76*** , 1363-1398 (1994).

[3] M. Ilegems, H. C. Montgomery, *J. Phys. Chem. Sol.* ***34*** , 885 (1973).

[4] H. P. Maruska, J. J. Tietjen, *Appl. Phys. Lett.* ***15*** , 327 (1969).

[5] W. Seifert, R. Franzheld, E. Butter, H. Subotta, V. Riede, *Cryst. Res. and Tech.* ***18*** , 383 (1983).

[6] W. Gotz, N. M. Johnson , C. Chen, H. Liu, C. Kuo, W. Imler , *Appl. Phys. Lett.* ***68*** , 3144-3146 (1996).

[7] DK Gaskill, AE Wickenden, K Doverspike, B Tadayon, LB Rowland, *J. Electron. Mater.* ***24*** , 1525-1530 (1995).

[8] W. Gotz, N. M. Johnson, D. P. Bour, M. D. McCluskey, E. E. Haller, *Appl. Phys. Lett.* ***69*** , 3725 (1996).

[9] Shuji Nakamura, Naruhito Iwasa, Masayuki Senoh, Takashi Mukai, *Jpn. J. Appl. Phys.* ***31*** , 1258-1266 (1992).

[10] M. E. Lin, G. Xue, G. L. Zhou, J. E. Greene, H. Morkoc , *Appl. Phys. Lett.* ***63*** , 932-933 (1993).

[11] K. Pakula, Jacek M. Baranowski , M. Leszczy˜ski, B. Suchanek, M. Wojdak, *MRS Internet J. Nitride Semicond. Res.* ***3***, 23 (1998).

[12] R. Dwilinski, J. M. Baranowski, M. Kami˜ska, R. Doradzi˜ski, J. Garczy˜ski, L. Sierzputowski, *Acta Phys. Pol. A* ***90*** , 763 (1996).

[13] E. R. Glaser, T. A. Kennedy, K. Doverspike, L. B. Rowland, D. K. Gaskill , J. A. Freitas, Jr., M. Asif Khan, D. T. Olson, J. N. Kuznia , D. K. Wickenden , *Phys. Rev. B* ***51*** , 13326-13336 (1995).

[14] M. Kunzer, U. Kaufmann, K. Maier, J. Schneider, N. Herres, I. Akasaki, H. Amano, *Sci. Forum* ***143/147*** , 87 (1994).

FIGURES

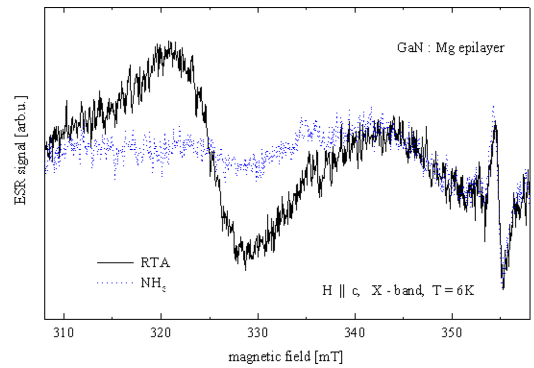

Figure 1. The ESR spectra of Mg-acceptor in GaN crystal after two thermal annealing procedures: RTA (solid line), and annealing in NH_3 atmosphere (dotted line). Microwave power P = 2 mW, modulation amplitude A = 0.2 mT. The narrow resonance line at higher magnetic field is due to the quartz sample holder.

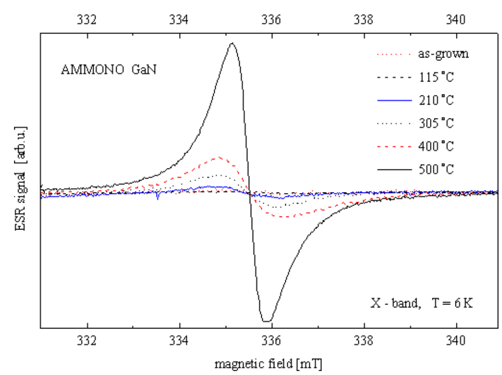

Figure 2. The ESR resonance line for g = 2.0026 in AMONO GaN crystals, observed after thermal annealing. Microwave power P = 2 mW, modulation amplitude A = 0.03 mT.

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