Optical Materials 33 (2011) 1041–1044

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Microscopic structure and energy transfer of vacancy-related defect pairs with Erbium in wide-gap semiconductors

A. Konopka [a,*], S. Greulich-Weber [a], V. Dierolf [b], H.X. Jiang [c], U. Gerstmann [a], E. Rauls [a], S. Sanna [a], W.G. Schmidt [a]

[a] University of Paderborn, Warburger Str. 100, 33098 Paderborn, Germany
[b] Center for Optical Technologies, Lehigh University, Bethlehem, PA 18015, USA
[c] Department of Electrical & Computer Engineering, Texas Tech University, Lubbock, TX 79409, USA

ARTICLE INFO

Article history:
Received 4 June 2010
Received in revised form 9 December 2010
Accepted 15 December 2010
Available online 12 February 2011

Keywords:
Erbium
SiC
GaN
EPR

ABSTRACT

Electron Paramagnetic Resonance (EPR) measurements of Erbium-doped 6H–SiC and wurtzite GaN samples are compared to total energy calculations based on density functional theory (DFT) in order to investigate the well-known luminescence of the intra 4*f*-shell transition at 1540 nm, useful in light-emitting diodes or lasers. The highly correlated *f*-electrons of Erbium (Er) have been treated within an LDA+U approach. We discus how pairs of an Er-ion with intrinsic defects can be responsible in GaN and SiC for relaxing the selection rules for intra 4*f*-shell transitions: In GaN our EPR investigation indicates the presence of a nitrogen vacancy next to the Er-ion. Through controlled generation of intrinsic defects in 6H–SiC single crystals and EPR measurements we support the corresponding model in SiC, that predicts defect pairs of an Er-ion and a neighboring carbon vacancy. In other words, low-energy irradiation seems to be a promising way to enhance the Er-luminescence desired for device applications.

1. Introduction

Rare earth (RE) doped semiconductors are attracting an increasing interest due to their potential use as light-emitting diodes or lasers. Of particular interest are Er-ions since their intra 4*f*-shell transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ observed at 154 nm coincides with the minimum absorption of typical silica-based optical fibers. Since the strongly localized electrons of the 4*f*-shell are efficiently shielded by the outer closed shells, the interaction of the RE-ion and the surrounding host atoms is very weak. Thus, the wavelength of the RE-transition is practically independent on the material, and any semiconductor can be used as a possible host material. The main problem of a rather low luminescence at room temperature, however, becomes less critical with an increasing fundamental gap of the semiconductor. In this respect, wide-gap semiconductors like SiC or GaN are superior to silicon [3]. The electronic structure of the RE luminescent centers as well as their excitation and emission mechanisms, however, are still under debate [9,8,7]. The screening of the outer shells makes a direct excitation of the 4*f*-electrons difficult; in the free ions the intra 4*f*-shell transitions are actually forbidden by the Laporte selection rules. Nonetheless, the presence of nearby intrinsic defects [5] may reduce the local symmetry and help this process by relaxing the selection rules. Despite many efforts, however, no luminescence band has been definitively assigned to a particular lattice site or a specific microscopic structure.

In this work, the microscopic structure of Er-related defect states in GaN and SiC is investigated via EPR measurements. Together with LDA+U total energy calculation in the framework of DFT, defect pairs with the Er-ion on the large lattice site (Ga, Si) and a neighboring (N, C) vacancy are found as the most likely candidates, whereby in SiC low-energy irradiation is shown to activate the Er-related EPR spectra.

2. Experimental details

Electron Paramagnetic Resonance (EPR) measurements are performed on GaN and SiC doped with Erbium. The GaN sample was grown by metal organic chemical vapor deposition (MOCVD) and in situ incorporation of Erbium [16]. The SiC sample was a nitrogen doped *n*-type epitaxial layer implanted by Erbium [3]. It was electron irradiated in two steps to analyze the influence of intrinsic defects and to investigate the creation of defect complexes with the incorporated Er-ions. The first electron irradiation with 200 keV was done by a Jeol 2000FX electron microscope at a flux of about 10^{20} cm^{-2}. A second electron irradiation was done elsewhere with an energy of 10 MeV at a flux of 10^{17} cm^{-2}.

In all samples, the thickness of the Er-doped layer is below 1 μm. Considering the lateral dimensions of the active volume,

* Corresponding author.
E-mail address: konopka@physik.uni-paderborn.de (A. Konopka).

0925-3467/$ - see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.optmat.2010.12.005

the total number of spins can be estimated to 10^{15} in the GaN sample and 10^{12} in the SiC sample. Hence, an EPR signal intensity equivalent to a concentration of 10^{16} cm^{-3} for the GaN sample and a very low value of 10^{12} cm^{-3} for the SiC sample are expected. The EPR experiments were carried out with a custom-built X-band (9.87 GHz) spectrometer with a He gas flow cryosystem between 5 K and 300 K. A 100 kHz field modulation in combination with lock-in detection has been applied for signal improvement.

3. Results and discussion

Fig. 1 shows an EPR spectrum of the Er-doped GaN sample measured at 6 K. For $\vec{B} \| \vec{c}$, the spectrum consists of fourfold hyperfine-split resonance lines resolved around 240 mT. For $\vec{B} \perp \vec{c}$, this resonance is unsplit and shifted to much lower magnetic fields (about 65 mT) suggesting an extremely anisotropic g-factor. Thus, intrinsic defects can be excluded and the presence of some impurity atoms with large spin-orbit coupling has to be assumed. This, together with the intentional Er-doping, strongly indicates the participation of an Er-ion in the responsible defect structure. A closer look at the four resonance lines shows that they consist of a superposition of two sets of slightly different splittings, which can be explained by the different nuclear g_N-factor of the two Ga isotopes with nuclear spin $I = 3/2$ (see also inset of Fig. 1) and similar natural abundance (60.1% and 39.9% for ^{69}Ga and ^{71}Ga, respectively). The form of the resonance lines is determined by the central line caused by the Er nuclei without nuclear spin. The eight lines caused by the hyperfine interaction of ^{167}Er with a nuclear spin of $I = 7/2$ should provide almost the same splitting as those observed in Ref. [10], but they have only some percent of the intensity of the central Er-lines, and thus cannot be resolved.

In solids, *isolated* Er-ions are incorporated as trivalent ions in all known cases. Whereas the charge state depends on the given host material (e.g. neutral in case of GaN, singly negative for SiC), the resulting electron configuration is always $4f^{11}6s^0$. According to our total energy calculation, the 4*f*-shell is strongly spin-polarized. As a result, the spin-up channel is filled-up completely before the remaining *f*-electrons occupy the spin-down states, resulting in three unpaired *f*-electrons and a total spin of $S = 3/2$. From this, a full set of EPR parameters can be extracted with the help of the following Spin-Hamiltonian

$$\mathcal{H} = \mu_B \vec{B} \cdot \mathbf{g} \cdot \vec{S} + \vec{S} \cdot \mathbf{D} \cdot \vec{S} + \sum_{i=1}^{N} \vec{I}_i \mathbf{A}_i \vec{S}, \quad (1)$$

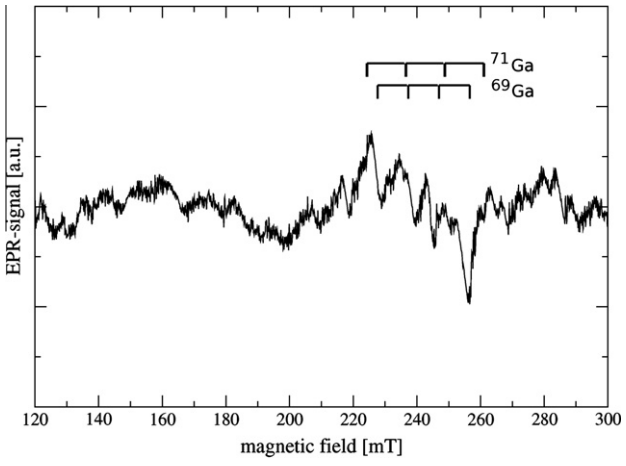

Fig. 1. EPR spectrum of Er-doped GaN sample measures at 6 K with the magnetic field parallel to the *c*-axis: hyperfine splitting of central Er-ines by the two Ga isotopes with nuclear spin ($I = 3/2$).

Table 1
Spin-Hamilton parameters for the Er-related defect in GaN. The hyperfine splittings A are given for ^{69}Ga, those for ^{71}Ga are a factor of 1.2706 larger. $A_\perp$ is estimated from the linewdth of the unsplit EPR resonance line. The spectra are due to a defect center with total spin $S = 3/2$. For comparison, the corresponding values for an *effective* spin $S_{\text{eff}} = 1/2$ are also given. Note, that the hyperfine splittings do not depend on the total spin used within the fitting process.

Parameter	$S = 3/2$	$S_{\text{eff}} = 1/2$
D	Very large	0
$g_\parallel$	0.984 ± 0.002	2.952 ± 0.005
$g_\perp$	2.935 ± 0.002	8.806 ± 0.005
^{69}Ga $A_\parallel$[MHz]	266.6 ± 0.3	266.6 ± 0.3
^{69}Ga $A_\perp$[MHz]	<25	<25

determined by the electronic **g**-tensor, the fine structure (zero-field splitting **D**), and the hyperfine structure $\mathbf{A}_i$ [15]. For two different orientations of the applied magnetic field, the EPR parameters are listed in Table 1. The data in the left column is obtained assuming a high-spin state and a very large zero-field splitting D caused by spin-orbit coupling within the Erbium 4*f*-shell. As a result, the different sublevels are well separated and a spin-flip is induced between the $m_s = -1/2$ and $m_s = +1/2$ sublevels of the spectra. Since from EPR experiments alone the total spin remains unknown, an effective spin $S_{\text{eff}} = 1/2$ is often assumed in the literature, resulting in by a factor of three larger g-values, given by $g_\parallel = 2.952$ and $g_\perp = 8.806$ (see right column of Table 1). In 6H–SiC, similar *effective* values for $g_\perp$ (8.28 and 8.07) are reported for axial Er-related spectra [1].

DFT-based total energy calculations have shown that an incorporation of an Er-ion at the nitrogen sublattice is very unlikely [11]. If a Er-ion is inserted in a divacancy, the resulting defect is always a $Er_{Ga}V_N$ pair, independent of the position the Er-ion has been started from: without any barrier the Er-ion relaxes to its preferred lattice position on a Ga-site.

In hexagonal GaN, the Ga-site itself provides C_{3v} symmetry. Although an isolated incorporation of the Er-ion leads to a considerable outward relaxation of the N-ligands, the Er-ion stays exactly on-center [11], even reducing the difference in the axial and non-axial bondlegths (−0.03 Å) if compared with that for the ideal hexagonal crystal (−0.05 Å). Thus, similar to 3*d*-transition metal ions [4], the isolated Er-ions resemble those in the cubic polytype.

In other words, the original hope that the hexagonality of the host material alone could be sufficient to relax the selection rules enhancing the RE-luminescence is not fulfilled at all. So, an additional lattice distortion is necessary to lower the symmetry in order to relax the selection rules considerably. Nearby intrinsic defects like vacancies and self-interstitials can provide such lattice distortion [11]. Complexes of Er and Ga-interstitials have been calculated to provide binding energies above 1 eV, but very high formation energies above 20 eV. Nitrogen vacancies and gallium vacancies (Fig. 2) are more promising alternatives, forming stable,

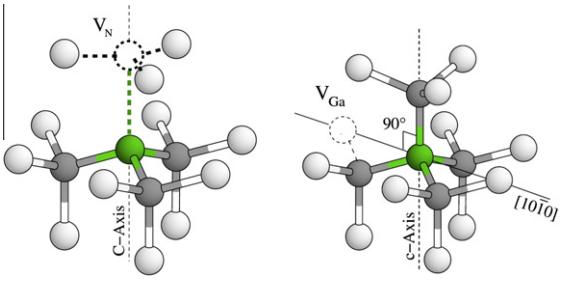

Fig. 2. Microscopic structure of Er-related defect pairs with nearby vacancies: $Er_{Ga}V_N$ pair (left), next nearest Er_{Ga}–V_{Ga} pair (right).

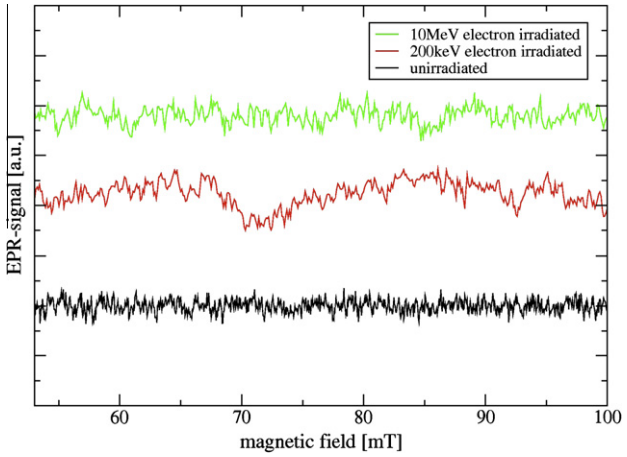

Fig. 3. EPR spectra of Er-doped 6H–SiC samples after electron irradiation with different energies. The spectrum of the 200 keV irradiated sample show a weak EPR signal that cannot be seen in the both other spectra (unirradiated as well as irradiated with high-energy electrons). The spectra were taken at 6 K with $\vec{B} \perp \vec{c}$.

strongly bound defect pairs with Er-ions. From the energetically point of view the Er_{Ga}–V_{Ga} pair is slightly favored. It is known, however, that the hyperfine splittings caused by the next nearest ^{69}Ga nuclei surrounding a gallium vacancy are comparatively small and most important *isotropic* [2]. Thus, a nearby Ga vacancy can hardly explain the extremely *an*isotropic hyperfine splitting reported in this work. The $Er_{Ga}V_N$ *nearest* neighbor pair, however, shows Ga ligands with sp^3-hybridized dangling bonds, naturally providing *strongly anisotropic* hyperfine splittings. Presently, it gives the most probable explanation for the observed Er-related EPR spectrum in α-GaN.

In 6H–SiC, our investigations are based on a controlled generation of intrinsic defects in Er-doped samples by low and high-energy electron irradiation, and subsequent EPR measurements. Fig. 3 shows the resulting spectra. While the Er-implanted sample shows no typical luminescence at 1540 nm and no Er-related EPR-signal (*black line*), after low-energy irraditaion with 200 keV an additional EPR signal appears at about 68 mT (*red line*[1]). After a second irradiation with high-energy (10 MeV) electrons, this EPR signal is no longer observed (*green line*), and known EPR signals of irradiation-induced intrinsic defects, dominated by the isolated silicon vacancy V_{Si}^{-} appear instead. Irradiation induced defects in SiC have been already frequently investigated: While high-energy irradiation is known to produce various silicon-related vacancies depending critically on the irradiation conditions and details of the post-irradiation annealing (see e.g., [14,12,13]), low-energy electrons are only able to remove the comparatively light carbon atoms from their lattice sites. This indicates that the observed EPR signal in Fig. 3 is most probably related to a defect that incorporates a carbon vacancy. Because of the extremely anisotropic *g*-factor (for B‖c the resonance moves to higher magnetic field where it is no longer resolved due to line-broadening by hyperfine splitting) an isolated carbon vacancy can be excluded and the presence of an Er-ion has to be assumed.

The low absolute number of spins in the sample causes an extremely weak EPR intensity. The corresponding spin density of 10^{-12} cm^{-3} is hardly in the detection limit of the conventional EPR spectrometer. This leads to the non-Gaussian line form and makes an accurate determination of the *g*-factor difficult. Nevertheless, a rough estimate gives a *g*-factor of about 10.4 (±0.2) if analized with an effective spin $S_{eff} = 1/2$. This value is in good agreement

[1] For interpretation of color in Fig. 3, the reader is referred to the web version of this article.

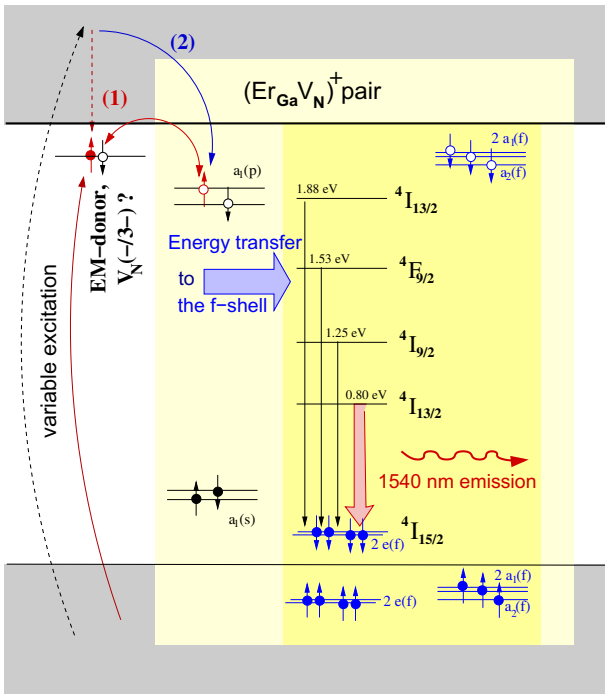

Fig. 4. Possible excitation mechanism of $(Er_{Ga}V_N)^+$ in GaN: (1) via an assistant level given by an effective mass (EM) donor, a transition level of the nitrogen vacancy V_N or (2) self-assisted via an unoccupied, vacancy-like level of the $Er_{Ga}V_N$ pair. In case of an assistant level, the energetic distances to the conduction bands determine possible low and high temperature limits of the luminescense. The energy of the Er-multiplets $^{2S+1}I_J$ are taken from atomic calculations.

with Er-related EPR signals with $g_x = 10.6$ already reported in 6H–SiC before: in the light of our results, the three orthorombic signals of unknown microscopic origin reported in Ref. [1] can be explained by the three inequivalent non-axial pairs in 6H–SiC [6].

In wide-gap semiconductors, in α-GaN as well as in 6H–SiC, we have detected Er-related EPR spectra which can be explained by nearest neighbor Er-vacancy pairs. There are further similarities in the electronic structures, which are crucial for an efficient luminescence of the Er-ions: In both materials, the Er-vacancy pair induces an additional defect level close to the conduction band minima. By this, delocalized conduction band electrons generated e.g. by illumination with above-band light, can be captured close to the Er-ion. The remaining step required for the Er-luminescence is an efficient energy transfer to the shielded 4*f*-electron shell (see Fig. 4). Alternatively to this self-assistant excitation mechanism, the electron capture could be mediated by some nearby isolated vacancies or effective mass donors serving as assistant levels. In this case, the luminescence should show a pronounced temperature dependence (see e.g. [5]): before an energy transfer to the *f*-shell becomes possible, the electron captured by the assistant level has to be transfered to the Er-vacancy pair, most probably by a thermal activation via the conduction bands.

A direct correlation between the Er-vacancy pairs responsible for the observed EPR-spectra and the desired RE-luminesence, however, remains still an open question. An ultimative investigation of such a correlation would be possible by detecting the EPR directly in the optical channel of the luminescence (PL-EPR), a measurement which remains for next future work.

References

[1] P.G. Baranov, I.V. Ilyin, E.N. Mokhov, A.B. Pevtsov, V.A. Khramtsov, Phys. Solid State 41 (1999) 32.
[2] K.H. Chow, L.S. Vlasenko, P. Johannesen, C. Bozdog, G.D. Watkins, A. Usui, H. Sunakawa, C. Sasaoka, M. Mizuta, Phys. Rev. B 69 (2004) 089905.

[3] W.J. Choyke, R.P. Devaty, L.L. Clemen, M. Yoganathan, G. Pensl, C. Hässler, Appl. Phys. Lett. 65 (1994) 1668.
[4] U. Gerstmann, A.T. Blumenau, H. Overhof, Phys. Rev. B 63 (2001) 075204.
[5] U. Gerstmann, E. Rauls, S. Sanna, T. Frauenheim, H. Overhof, Mater. Sci. Forum (2006) 529–655.
[6] U. Gerstmann, A.P. Seitsonen, D. Ceresoli, F. Mauri, H.J. von Bardeleben, J.L. Cantin, J. Garcia Lopez, Phys. Rev. B 81 (2010) 195208.
[7] A. Kozanecki, V. Glukhanyuk, H. Przybyliska, Phys. Status Solidi A 205 (1) (2008) 38–42.
[8] H.J. Lozykowski, W.M. Jadwisienczak, Phys. Status Solidi B 244 (2007) 2109.
[9] K. O'Donnell, B. Hourahine, Eur. Phys. J. Appl. Phys. 36 (2006) 91.
[10] M. Palczewska, A. Wolos, M. Kaminska, I. Grzegory, M. Bockowski, S. Krukowski, T. Suski, S. Porowski, Solid State Commun. 114 (2000) 39.
[11] S. Sanna, W.G. Schmidt, T. Frauenheim, U. Gerstmann, Phys. Rev. B 80 (2009) 104120.
[12] M.V.B. Pinheiro, E. Rauls, U. Gerstmann, S. Greulich-Weber, J.-M. Spaeth, Phys. Rev. B 70 (2004) 245204.
[13] A. Scholle, S. Greilich-Weber, E. Rauls, W.G.S. Schmidt, U. Gerstmann, Mater. Sci. Forum (2010) 403–648.
[14] N. Son, M. Wagner, C. Hemmingsson, L. Storasta, B. Magnusson, W. Chen, S. Greulich-Weber, J.-M. Spaeth, E. Janzen, in: Electronic Structure of Deep Defects in SiC, Springer, Berlin, Heidelberg, 2004.
[15] J.-M. Spaeth, H. Overhof, Point Defects in Semiconductors and Insulators, Springer-Verlag, Heidelberg, 2003.
[16] C. Ugolini, N. Nepal, J.Y. Lin, H.X. Jiang, J.M. Zavada, Appl. Phys. Lett. 89 (2006) 151903.