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


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 4f-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 discuss how pairs of an Er-ion with intrinsic defects can be responsible in GaN and SiC for relaxing the selection rules for intra 4f-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.

Keywords:
Erbium
SiC
GaN
EPR

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 4f-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 4f-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 4f-electrons difficult; in the free ions the intra 4f-shell transitions are actually forbidden by the Laporte 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 \( 10^{20} \text{ cm}^{-2} \). A second electron irradiation was done elsewhere with a flux of about \( 10^{17} \text{ cm}^{-2} \).

In all samples, the thickness of the Er-doped layer is below 1 \( \mu \text{m} \). Considering the lateral dimensions of the active volume,
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 \(10^{16}\,\text{cm}^{-3}\) for the GaN sample and a very low value of \(10^{12}\,\text{cm}^{-3}\) 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 \(B \parallel z\), the spectrum consists of fourfold hyperfine-split resonance lines resolved around 240 mT. For \(B \perp z\), 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 \(g_E\)-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 \(^{69}\text{Ga}\) and \(^{71}\text{Ga}\), 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 \(^{167}\text{Er}\) 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 4\(f^6\)6\(s^0\). According to our total energy calculation, the 4\(f^6\) 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

\[
\mathcal{H} = \mu_B B \cdot S + D \cdot S + \sum_{i=1}^{N} I_i A_i \cdot S,
\]

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(S = 3/2)</th>
<th>(S_n = 1/2)</th>
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<tbody>
<tr>
<td>(D)</td>
<td>Very large</td>
<td>0</td>
</tr>
<tr>
<td>(g_i)</td>
<td>(0.984 \pm 0.002)</td>
<td>(2.952 \pm 0.005)</td>
</tr>
<tr>
<td>(g_i)</td>
<td>(2.935 \pm 0.002)</td>
<td>(8.806 \pm 0.005)</td>
</tr>
<tr>
<td>(^{69}\text{Ga}) (A_i) [MHz]</td>
<td>(266.6 \pm 0.3)</td>
<td>(266.6 \pm 0.3)</td>
</tr>
<tr>
<td>(^{71}\text{Ga}) (A_i) [MHz]</td>
<td>&lt;25</td>
<td>&lt;25</td>
</tr>
</tbody>
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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-iners by the two Ga isotopes with nuclear spin \(I = 3/2\).

Fig. 2. Microscopic structure of Er-related defect pairs with nearby vacancies: Er\(_{\text{Ga}}\)\(_{\text{V}}\) pair (left), next nearest Er\(_{\text{Ga}}\)-\(_{\text{V}}\) pair (right).
strongly bound defect pairs with Er-ions. From the energetically point of view the ErGa–VGa pair is slightly favored. It is known, however, that the hyperfine splittings caused by the next nearest \(^{60}\)Ga nuclei surrounding a gallium vacancy are comparatively small and most important \textit{isotropic} [2]. Thus, a nearby Ga vacancy can hardly explain the extremely anisotropic hyperfine splitting reported in this work. The ErGa–VGa nearest neighbor pair, however, shows Ga ligands with \(sp^3\)-hybridized dangling bonds, naturally providing \textit{strongly anisotropic} hyperfine splittings. Presently, it gives the most probable explanation for the observed Er-related EPR spectrum in \(\alpha\)-GaN.

In \(\alpha\)-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 irradiation with 200 keV an additional EPR signal appears at about 68 mT (red line). 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 \(V_s\) 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 \(B\parallel c\) 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 analyzed with an effective spin \(S_{\text{eff}} = 1/2\). This value is in good agreement with Er-related EPR signals with \(g_s = 10.6\) already reported in \(\alpha\)-SiC before: in the light of our results, the three orthorhombic signals of unknown microscopic origin reported in Ref. [1] can be explained by the three inequivalent non-axial pairs in \(\alpha\)-SiC [6].

In wide-gap semiconductors, in \(\alpha\)-GaN as well as in \(\alpha\)-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 in-duction of the \(4f\)-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 transferred 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-luminescence, 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


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