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ZEEMAN STUDY OF THE 0.9 eV EMISSION IN AlN AND GaN

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Abstract: We investigate the magnetooptical properties of the 0.9 eV luminescence in AlN and GaN. The zero-phonon lines at 0.943 eV in AlN and at 0.931 eV in GaN are attributed to transitions within a d^2-configuration, because of a characteristic threefold ground-state splitting in magnetic fields. For AlN we determine a g-value of 1.96±0.07 and a zero-field splitting of 120±30 μeV for the $^3A_2(F)$ ground state. On the basis of the temperature dependence in a magnetic field, we attribute the 0.943 eV zero-phonon line in AlN to the $^1E(D)$-$^3A_2(F)$ transition and the 0.931 eV zero-phonon line in GaN to the $^3T_2(F)$-$^3A_2(F)$ transition of isolated V^{3+}. The different fine-structure of the excited state in AlN and GaN is explained in a Tanabe-Sugano diagram.

Introduction

Despite the enormous progress in growth and device technology there is only little information about deep defects in group III-nitrides. Transition metals (TMs) form deep defects and can be expected to be common contaminations of these materials which are grown at very high temperatures. In spite of their technological relevance for growing high resistivity material, not much detailed information on TM defects is available up to now.
Usually, the TMs are incorporated substitutionally on the metal-cation site in III-V compounds. Thus, the neighborhood of the TM is given by four nitrogen atoms. Because of the localized wavefunction of the deep impurity and the similar lattice constants of GaN and AlN together with their large bandgaps, it is expected that internal transitions of the same transition metal element appear at about the same energy. Up to now, five TM luminescence bands have been reported for both GaN and AlN and they are compared in [1] .
On the basis of magnetooptical measurements, the electronic configurations of the 1.30 eV and 1.19 eV TM defects in GaN were identified. The 1.30 eV luminescence is unambiguously attributed to the $^4T_1(G)$-$^6A_1(S)$ transition of Fe^{3+} ($3d^5$-system) [2,3], whereas the 1.19 eV zero-phonon line (ZPL) is attributed to the $^1E(D)$-$^3A_2(F)$ transition of a d^2-system [4]. Ti^{2+} and Cr^{4+} are discussed as luminescence centers [4,5]. No other magnetooptical measurements have been performed so far. For GaN, the ZPLs at 0.931 eV and 0.82 eV are attributed to V^{3+} [5] or TM-complex centers [1]. Analogous assignments have been performed for the ZPLs at 1.297 eV, 1.201 eV, 1.043 eV, 0.943 eV and 0.797 eV in AlN [1]. No Zeeman data were published for AlN up to now. In this paper we report on the first Zeeman study of the 0.943 eV ZPL in AlN and the 0.931 eV ZPL in GaN.

Experimental Results

The AlN samples were grown by mixing Al and N at very high temperatures (1900°C). Small AlN crystalline needles were obtained with a typical length of 3 mm and a diameter of about 100 μm. The GaN sample investigated here was epitaxially grown on (0001) sapphire by Hydride Vapour Phase Epitaxy. The sample was 400 μm thick and has n-type conductivity. Photoluminescence (PL) was excited by various lines of an Ar^+ or Kr^+ laser. The Zeeman PL experiments were carried out using a superconducting 15 T magnet built in split-coil configuration. All Zeeman

measurements were done in Faraday configuration (H||k). The luminescence was detected by a cooled Ge photodiode.

Figure 1 shows typical luminescence spectra of the AlN and GaN samples at T= 1.8 K. For GaN, the 1.30 eV, the 1.19 eV and the 0.93 eV emission bands are observed, when exciting the samples with the 2.61 eV emission line of the Ar^+ laser. For AlN, only the 0.94 eV and the 0.79 eV luminescence is detected using the blue/green lines of the Ar^+ laser for excitation. With 1.92 eV excitation, the 1.2 eV and the 1.05 eV luminescence are also observed in AlN. The 1.297 eV ZPL is not observed in our AlN samples. This indicates a different impurity content of the AlN samples compared to the AlN ceramics investigated by Baur *et al.* [5].

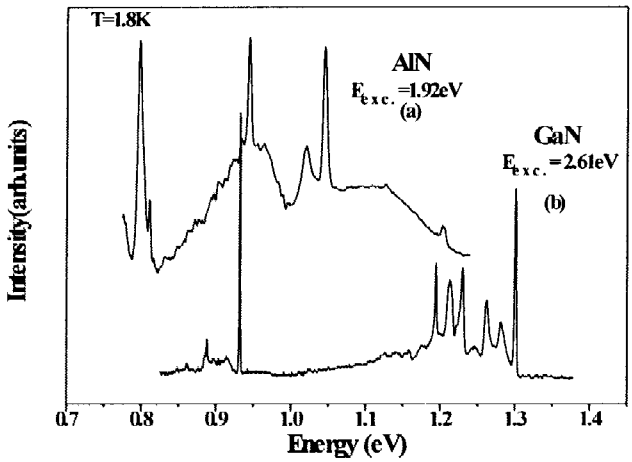

Figure 1: Photoluminescence spectra of AlN and GaN at T=1.8 K. The samples were excited at 1.92 eV (a) and at 2.61 eV (b), respectively.

The 0.9 eV ZPL in GaN and AlN

In order to investigate the fine-structure of the 0.9 eV ZPLs in AlN and GaN, we performed temperature dependent PL studies. Only for GaN a hot line 1.6 meV above the main peak at 0.931 eV is observed, whereas for AlN no hot lines could be detected. This indicates, that the excited state is a singulet for AlN and a doublet for GaN. No polarization effects could be detected. These results are in accordance with those of Pressel *et al.* [1] and Baur *et al.* [5].

High resolution spectra of the 0.943 eV ZPL in AlN for magnetic fields of 0 T, 9 T and 15 T are shown in figure 2. For 0 T, in addition to the main peak at 0.943 eV, a weak shoulder is detected on the low energy side. These structures can be fitted with two Gaussian lineshapes peaking at 0.94255 eV and 0.94170 eV. The full width at half maximum (FWHM) is 1.5±0.1meV for the main peak and 1.9±0.5 meV for the weak structure.

With increasing magnetic field, a threefold splitting of the main ZPL is observed above B= 7 T in the configuration H⊥c. The intensity ratio of the three lines does neither depend on the temperature nor on the magnetic field. This indicates that the splitting occurs in the ground state of the impurity. The splitting can be fitted with three Gaussian lineshapes with a FWHM of 1.5 meV for each peak. It is observed, that the energy splitting between the two high energy ZPLs of the three ZPLs is slightly larger than that of the two low energy ZPLs. This behavior indicates a zero-field splitting.

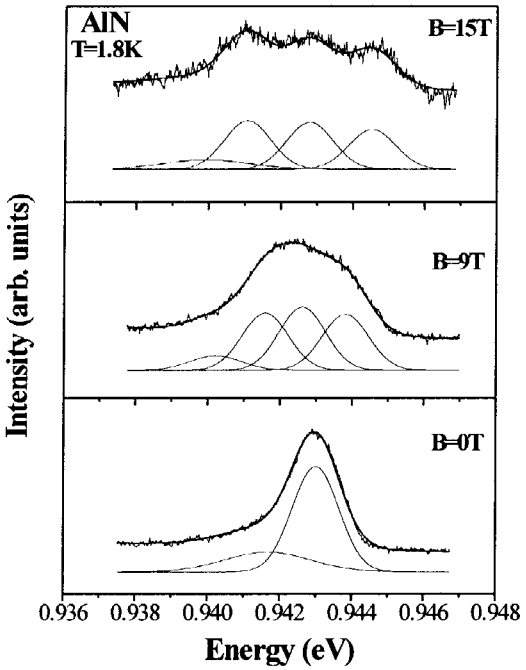

Figure 2: Zero-phonon line region of the 0.943 eV emission in AlN for different magnetic fields at T=1.8 K. The threefold splitting of the main ZPL is caused by the magnetic behavior of the $^3A_2(F)$ ground state.

The weak structure at 0.9417 eV, observed in spectrum at 0 T exhibits a broadening up to a FWHM of 2.8±0.5 meV at 15 T. This broadening corresponds to a g-value of 1.0±0.2, which indicates a different Zeeman-behavior compared to the main ZPL. However, due to the signal to noise ratio, the broadening could be larger, too. Possibly this shoulder is caused by internal strain or a disturbance in the neighborhood of the luminescence center.

The energy positions of the three fitted peaks in dependence on the magnetic field are summarized in Fig. 3. By fitting the data points in dependence on the magnetic field, it is clearly observed that a zero-field splitting of the ground state exists ($|D|=120\pm30$ μeV). Such a Zeeman behavior is a typical fingerprint for $^3A_2$ ground state of a d^2 configuration in trigonal symmetry usually detected by EPR measurements [10].

In order to check whether the spectra are isotropic, we rotated the AlN needle at B = 14 T from $H\perp c$ to $H\|c$. Within the margin of error, the Zeeman pattern did not depend on the rotation angle θ. Together with the almost symmetric Zeeman pattern (Fig. 3), this indicates that there is no Zeeman splitting of the excited state.

For GaN, only a broadening of the ZPL is observed in dependence on the magnetic field. This is mainly due to the larger FWHM of the ZPL (3 meV) in comparison to AlN and leads to a larger error of detection for GaN. However, the broadening of the 0.931 eV ZPL in GaN can be simulated assuming a threefold symmetrical splitting and using three identical Gaussian lineshapes with constant FWHM for all magnetic fields. This procedure results in an estimated g-value of 2.0±0.5 in agreement with that of the 0.943 eV emission in AlN.

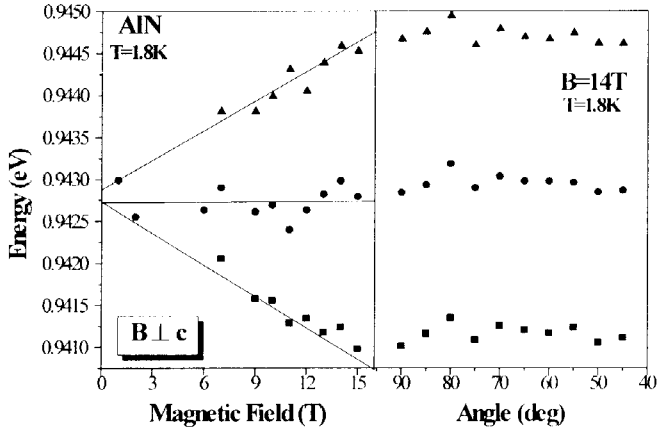

Figure 3: Zeeman behavior of the 0.943 eV ZPL for **B⊥c** (left) and angular dependence at B=14 T (right). The zero-field splitting of 120±30μeV together with the g-value of 1.96±0.07 is a fingerprint for the $^3A_2(F)$ ground state of V^{3+}.

Discussion

Taking into account the identical neighborhood of a TM impurity in both nitride compounds, one should expect similar ZPL energies in both compounds, if these ZPLs are due to the same TM. This is what we observed in the case of the 0.943 eV and 0.931 eV emissions in AlN and GaN, respectively. In the context of our results, cation-substitutional $V^{3+}(3d^2)$ is the most probable TM candidate for these ZPLs in AlN and GaN. However, the observed fine-structure of the impurity transition is slightly different for both host compounds (Fig. 4). For AlN, no hot line and no phonon sideband is observed for the 0.943 eV ZPL. Together with the isotropic threefold Zeeman splitting of the ground state it seems most probable to attribute this ZPL to a $^1E(D)$-$^3A_2(F)$ transition where the g-value of the excited state is smaller than 0.1. It is expected, that the electron-phonon coupling of such a transition is small for both the ground and excited state, explaining the missing of a phonon sideband. Such a weak phonon coupling is also observed for the 1.19 eV ZPL in GaN, which is caused by a $^1E(D)$-$^3A_2(F)$ transition [4]. As already mentioned by Baur *et al.* [5], a hot line 1.6 meV above the main ZPL at 0.931 eV is observed for GaN. For GaAs, GaP, and InP, vanadium correlated ZPLs between 0.73 and 0.83 eV have been assigned to the symmetry forbidden $^3T_2(F)$-$^3A_2(F)$ crystal field transition of V^{3+}. At higher sample temperatures hot ZPLs separated by 1.2 meV, 1.9 meV and 1.5 meV from the cold ZPL have been reported for these materials [7]. The analogy to the GaN PL data is obvious. The line position of the ZPL is mainly determined by the cubic crystal field strength (Dq), which increases with the ionicity of the host crystal. Therefore, the higher energy of the emission in GaN and AlN is not suprising. The hot ZPL in GaN can be explained by a moderately strong dynamic Jahn-Teller effect [7]: The first order spin-orbit interaction within the excited $^3T_2(F)$ state is quenched by electron-phonon coupling; thermal occupation of the upper level at elevated temperatures yields an additional hot ZPL. The splitting between the ZPLs is mainly determined by the spin-orbit coupling constant λ, which is characteristic for the incorporated impurity atom. The splitting of 1.6 meV in the GaN PL is in excellent agreement with the splittings observed for V^{3+} impurities in other III-V compounds. It is also expected that the electron-phonon coupling for the $^3T_2(F)$-$^3A_2(F)$ is stronger than for the $^1E(D)$-$^3A_2(F)$ transition, explaining the stronger phonon sideband in GaN.

The different fine-structures found for GaN and AlN can be explained in the context of a schematic Tanabe-Sugano diagram. For smaller crystal field strength (10 Dq), the $^3T_2$ state is below the $^1E(D)$ state (GaN-case), whereas for larger crystal fields, the $^1E(D)$ state is below the $^3T_2(F)$ state (AlN-case). Because of the smaller lattice constant of AlN compared to GaN, it is expected, that the crystal field strength (10 Dq) is slightly stronger in AlN. The crystal-field transition in both cases should be located near the crossover point of the $^3T_2(F)$ and $^1E(D)$ level in the schematic Tanabe-Sugano diagram.

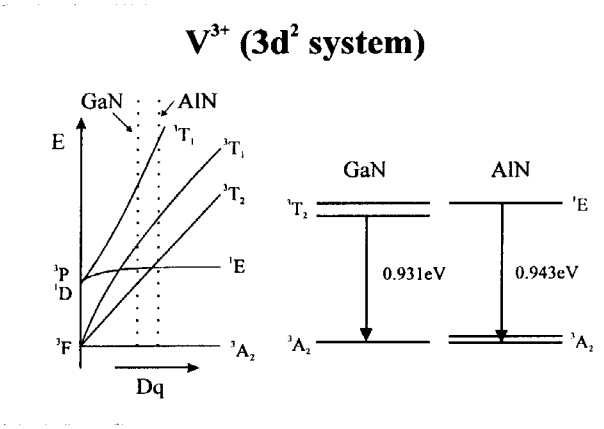

Figure 4: Schematic Tanabe-Sugano diagram for a $3d^2$-system together with the observed fine-structure for the V^{3+}-center in GaN and AlN. The larger crystal-field para-meter Dq for AlN is caused by the smaller lattice constant of AlN compared to GaN and explains the different fine structure of the excited states.

As mentioned above, the magnetoptical behavior (Fig. 3) of the 0.943 eV ZPL in AlN is a clear fingerprint for the $^1E(D)$-$^3A_2(F)$ transition. A zero-field splitting of $|D|=120\pm30$ μeV within the ground state is observed. In contrast to EPR, the sign of the splitting parameter D can be determined from the magnetooptical spectra. We obtain a positive sign for D and a g-value of 1.96 ± 0.07. These results are in good qualitative agreement with ZnO:V^{3+}. For ZnO:V^{3+}, a ground-state g-value of 1.93 and a zero-field splitting of D= +97 μeV were obtained [8,9]. The slightly larger D-value in GaN is due to the stronger covalent bonding compared to ZnO.

Similar trends for the zero-field splitting for the Fe^{3+} center in GaN compared to ZnO and ZnS are also known [3] (D=-8.84 μeV GaN, -7.38 μeV ZnO, -5.95 μeV ZnS). By comparing D for different d^2-systems in similar hosts, the spin-orbit coupling constant is the leading parameter for the magnitude of the zero-field splitting. A larger spin-orbit coupling constant λ should result in a larger D-value [10]. The free-ion value of λ increases from Ti^{2+} to V^{3+} and Cr^{4+} (λ=60 cm^{-1} (Ti^{2+}), 106 cm^{-1} (V^{3+}), 163 cm^{-1} (Cr^{4+})) due to the larger atomic number Z. It is expected, that the zero-field splitting is similar for identical TMs in AlN and GaN. It should be emphasized, that no zero-field splitting is observed for the magnetooptical measurements of the $^1E(D)$-$^3A_2(F)$ transition of the 1.19 eV luminescence in GaN which was attributed to Ti^{2+} [4] and Cr^{4+} [5] as well. As a consequence of the missing zero-field splitting, Ti^{2+} seems to be more probable than Cr^{4+} to explain the 1.19 eV ZPL in GaN. The observation of the zero-field splitting of the 0.943 eV ZPL in AlN is thus a further proof for the V^{3+} attribution in AlN and to the 0.931 eV ZPL in GaN. Unfortunately, the quality of Zeeman-data for GaN does not allow a direct estimation of a possible zero-field splitting of the 0.931 eV ZPL.

In order to prove the chemical nature of a defect, ion implantation of the corresponding TM is sometimes useful. However, the lattice damage and the creation of new defects during the implantation process makes the interpretation of the data difficult.

Recently, it was shown by Kaufmann *et al.* [6] that the implantation of vanadium in GaN followed by heat treatment gives rise to an intense PL emission at 0.82 eV. The center occurs in several

modifications caused by the radiation damage in the neighborhood of the impurity. No correlation between the 0.931 eV ZPL and the V doping is observed by these authors. This might indicate, that the charge state of the implanted V is different from the 3+ state. In the context of these results it is useful to compare these results with the properties of vanadium in ZnSe. Here, V^{3+}, V^{2+} and V^{+} can be observed in the same crystal, depending on the Fermi level position and on the excitation energy [11]. Thereby, the energy of the corresponding transition decreases from V^{3+} to V^{2+} and V^{+}. In this context it is also probable, that the 0.82 eV PL in GaN is related to V^{2+} or V^{+}. Also, V^{2+} with nearby radiation induced defects seems to be a reasonable interpretation for the 0.82 eV ZPL in GaN. Due to the fact, that our AlN needles also show the 0.797 eV ZPL, a vanadium correlation is also probable for these ZPLs. In summary, there is strong evidence to attribute the 0.943 eV ZPL in AlN and the 0.931 eV ZPL to recombinations within isolated V^{3+} centers.

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