

TRANSITION METAL LUMINESCENCE IN AlN CRYSTALS

K. PRESSEL*, R. HEITZ**, S. NILSSON*, P. THURIAN**, A. HOFFMANN**, B.K. MEYER***

*Institut für Halbleiterphysik, P.O.Box 409, 15204 Frankfurt(Oder), Germany

**Institut für Festkörperphysik, TU-Berlin, 10623 Berlin, Germany

***Physik-Department E16, TU-München, 85748 Garching, Germany

ABSTRACT

We study deep defects in AlN crystals in the near infrared by photoluminescence and compare the observed emissions with those in GaN. By below bandgap excitation with an Ar ion laser three no-phonon lines at 1.043 eV, 0.943 eV, and 0.797 eV were detected, which are caused by different residual transition metal contaminants. The weak emission at 1.043 eV and the intensive emission at 0.797 eV show AlN related phonon sidebands, whereas the emission at 0.943 eV has practically no phonon sideband. No hot lines could be detected for the emissions at 0.943 and 0.797 eV in temperature dependent measurements. We discuss possible identifications of the luminescence centers and the similarity between GaN and AlN in view of transition metals.

INTRODUCTION

With the tremendous increase of interest for GaN to develop not only a blue light emitting diode (LED) but also a blue laser, the interest in the nitrides increased in general. With the three nitride based semiconductors InN, GaN, and AlN the bandgap can be varied between 1.9 eV (bandgap of InN) and 6.3 eV (bandgap of AlN). Thus, not only the blue-green LED is possible [1], but also optical devices in the ultra-violet region. Up to now only a few photoluminescence (PL) studies of AlN have been done because no conventional ion lasers are available to excite electrons with 6.3 eV from the valence band to the conduction band. Deep defects like transition metals are believed to be omnipresent defects in the nitride compounds. However no quantitative information is available, yet. One method to gain information about deep traps also at low doping concentrations can be PL. For GaN various luminescence centers, which are caused by transition metals, were detected in the near infrared region (NIR) and could partly be identified [2-7]. Recently Baur et al. [4] reported two emission centers in AlN which have no-phonon (NP) lines at 1.201 eV and 1.297 eV. On the basis of a comparison of their results with two emissions at 1.19 eV and 1.3 eV in GaN they attributed the 1.201 eV luminescence center to Cr^{4+} and the 1.297 eV luminescence center to Fe^{3+} . Although we believe that the two emissions in GaN and AlN have the same origin, we attribute the 1.19 eV center in GaN [7] and therefore also the 1.201 eV center in AlN to the ${}^1E \rightarrow {}^3A_2$ internal electronic transition of Ti^{2+} and not to Cr^{4+} . In this paper we focus on further luminescence centers in AlN that could be detected in various crystals by below bandgap excitation with an Ar ion laser.

EXPERIMENTAL

The samples were partly 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 . For comparison we also investigated AlN powder and AlN layers grown by metal organic vapor phase epitaxy. Preliminary intentional doping experiments of GaN and AlN crystals by indiffusion of Fe at temperatures between 700 and 900°C in vacuum were unsuccessful to stimulate the Fe^{3+} luminescence signal at 1.3 eV in GaN and 1.297 eV in AlN.

The PL measurements were performed using either conventional monochromator technique or a BOMEM DA8.02 Fourier spectrometer. The excitation was performed with an Ar ion laser, which had a possible UV option. For all measurements a Germanium detector

was used.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows a PL spectrum of an AlN needle in the NIR. We observe one weak NP line at 1.043 eV and two intense NP lines peaking at 0.943 eV and 0.797 eV by below bandgap excitation with the 514 nm green line of the Ar ion laser. Only the 0.943 eV luminescence center could be detected under UV excitation, the other two emissions could not be detected by the UV light (360 nm) of the Ar laser.

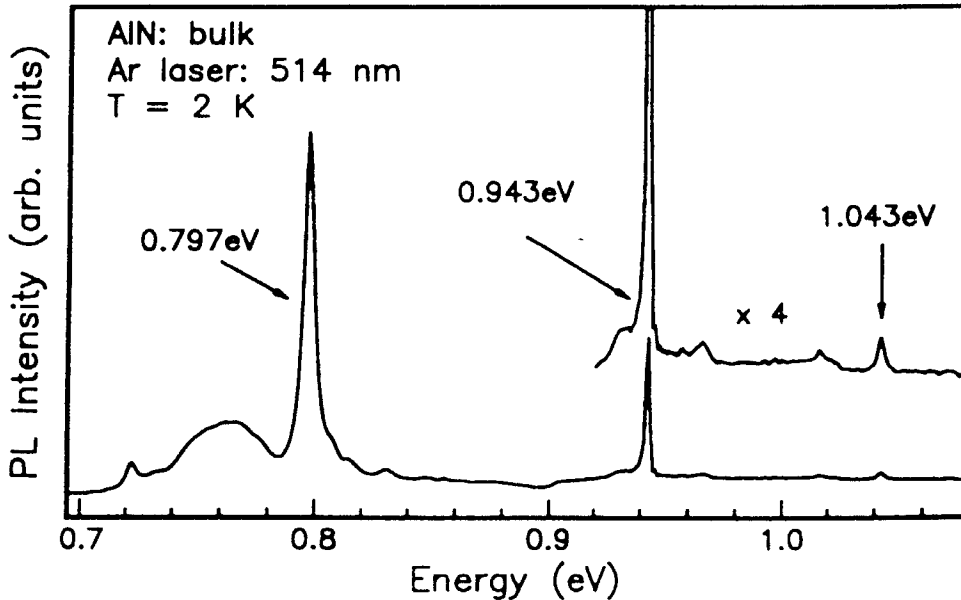


FIG. 1 NIR PL spectrum of an AlN crystalline needle excited with below bandgap excitation of the 514 nm green line of an Ar ion laser. Besides a weak NP line at 1.043 eV we observe two strong emissions peaking at 0.943 eV and 0.797 eV.

The 1.043 eV emission

Figure 2 (a) shows a more detailed spectrum of the weak 1.043 eV emission. The linewidth is about 2 meV. The defect center shows coupling to phonon modes close to modes observed for AlN in Raman spectroscopy [8]. The peaks in the phonon sideband at 86.3 meV, and 112.8 meV ($E_1(\text{LO})$) coincide with the modes observed in Raman spectroscopy on the AlN needles. The mode at 77.9 meV is a little lower in energy than the corresponding Raman mode. Thus, this mode is caused by a local mode of the defect. A part of the peak, which is attributed to the phonon at 112.8 meV, belongs to a shoulder of the 0.943 eV emission (see next section).

The 1.043 eV luminescence is still visible with about the same intensity at 80 K. We only observe a small shift of about 0.2 meV to lower energy, which is typical for internal electronic transitions of 3d elements [9]. As already pointed out in the introduction internal electronic transitions of the same transition metal ion in GaN and AlN seem to have nearly equal energies. On the basis of this argument the 1.043 eV emission in AlN is caused by the luminescence center responsible for the 1.047 eV emission in GaN[10, 11], which is depicted in the upper spectrum of Fig. 2. This emission is attributed to the ${}^4T_2 \rightarrow {}^4A_2$ transition of a 3d element with a $3d^7$ electronic configuration. Co^{2+} and Ni^{3+} are discussed as luminescence centers [10, 11].

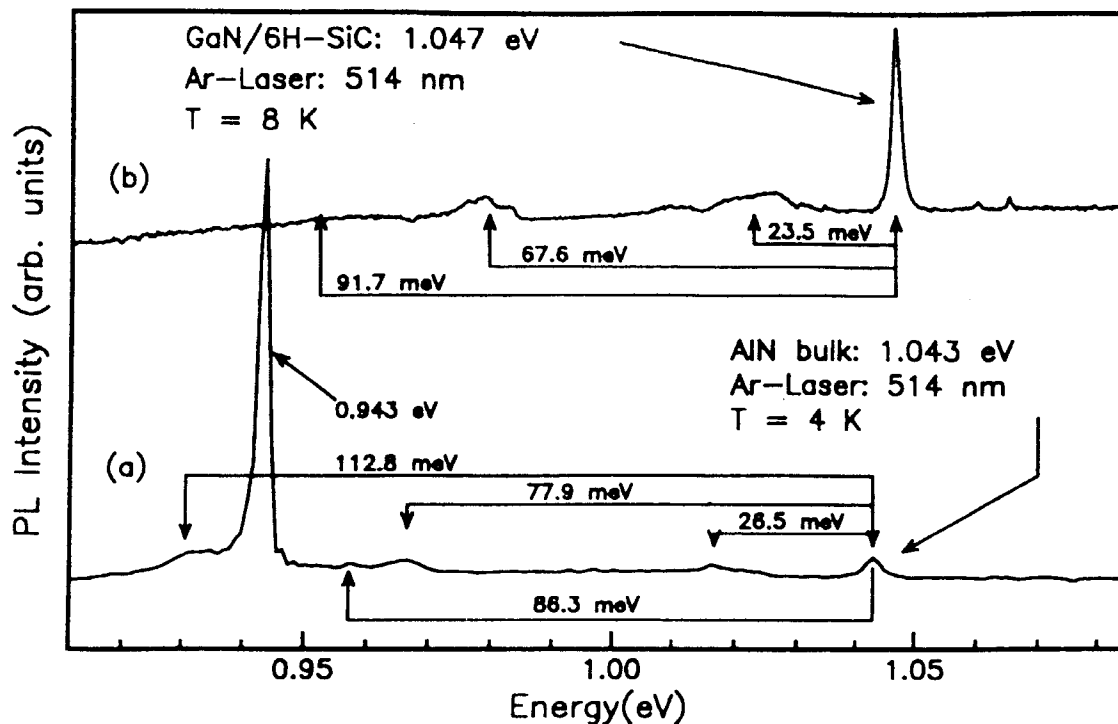


Fig. 2. (a) PL spectrum of the 1.043 eV emission in AlN together with the corresponding phonon sideband. The energy values belong to phonon energies and localized vibrational modes. (b) A comparison spectrum of the 1.047 eV luminescence in GaN together with the GaN related phonon sideband.

The 0.943 eV emission

The emission at 0.943 eV is close to an emission at 0.931 eV in GaN reported by Baur et al. [4]. They observed in temperature dependent PL spectra a hot line 1.6 meV higher in energy. This was their basis to attribute the 0.931 eV emission to an internal electronic transition of V^{3+} .

Figure 3 shows the 0.943 eV emission for three different samples. The inset compares two spectra recorded at different sample temperatures.

With rising temperature we observe no hot line (also at higher energies not shown here). The energy shift towards lower energy between the 2 K and the 85 K spectrum is about 0.2 meV. In some samples the emission showed a shoulder, labelled A, on the low energy side. A similar observation can be made for the 1.19 eV emission in GaN. Possibly this is caused by internal strain or rather a disturbance in the neighborhood of the luminescence center.

The linewidth of this emission is between 0.5 and 0.6 meV depending on the sample. For rising temperatures up to 85 K the linewidth only slightly increases from 0.5 meV to 0.7 meV.

Phonon sidebands could practically not be resolved for this emission. By chance the weak emission at 0.832 eV, labelled a (compare also Fig. 4), is 112.8 meV from the 0.943 eV NP line in this sample. But the emission at 0.832 eV belongs most definitely to a fine structure of the 0.797 eV luminescence center and not to the coupling of a phonon mode of AlN. The experimental behavior of this emission is very similar to that of the 1.19 eV emission in GaN and may also be caused by the ${}^1E \rightarrow {}^3A_2$ transition of a $3d^2$ configuration (possibly V^{3+} or Cr^{4+}). Maybe in AlN the 1E excited state is energetically below the 3T_2 excited state, similar to Ti^{2+} in GaN [7]. Zeeman measurements have to be performed to identify this emission center. The linewidth of 0.5 meV in the best samples is sufficient to allow these studies.

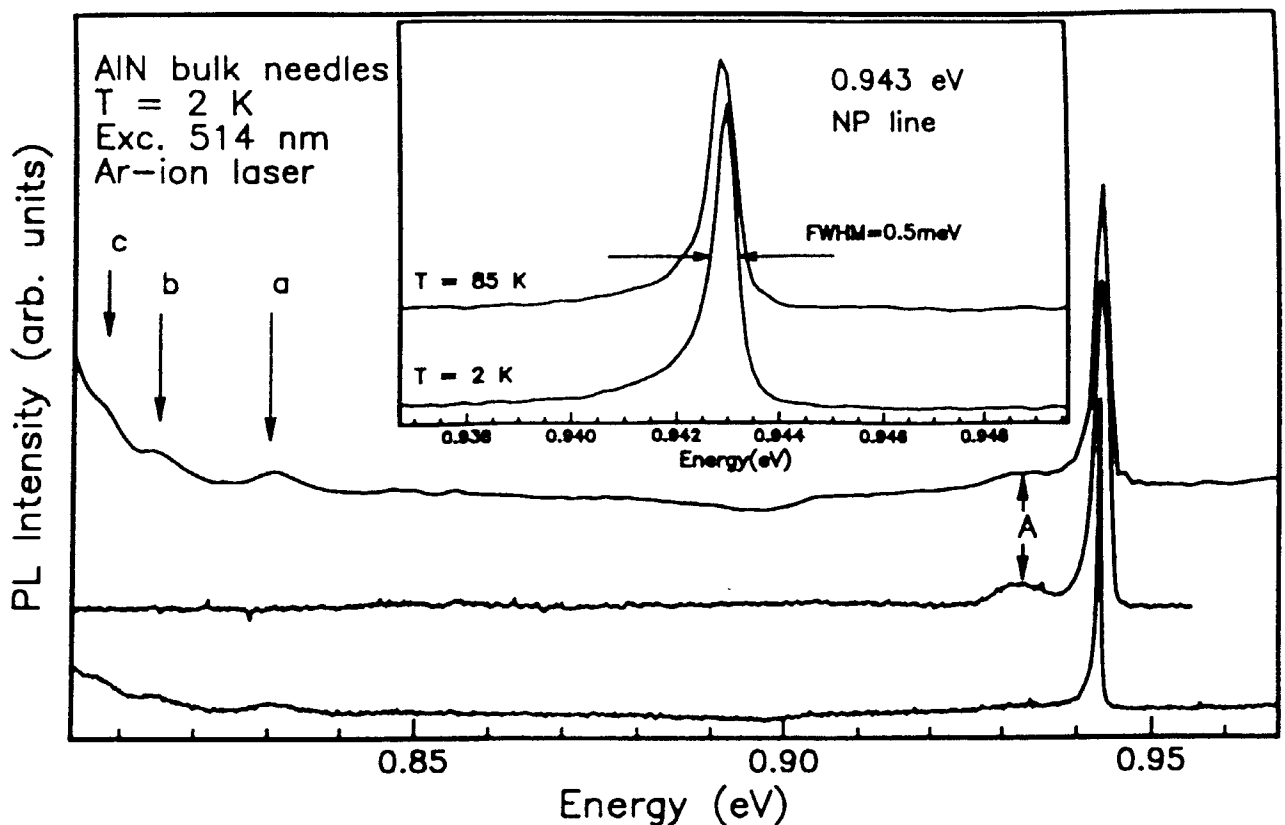


Fig. 3. PL spectra in the energy range of the 0.943 NP line. Spectra with and without the low energy shoulder labelled A are shown. In the inset two spectra detected at 2 K and 85 K are depicted. The linewidth of the peak is 0.5 meV.

The 0.797 eV emission

In general the strongest luminescence in our samples is the emission at 0.797 eV. Figure 4 gives a detailed spectrum in the range of this emission. Besides the strong NP line at 0.797 eV we resolve four weak satellite peaks in the range of the 0.797 eV emission at 0.832 eV (a), 0.815 eV (b), 0.811 eV (c), and 0.777 eV (e). The whole set of lines is indicated by the rake with five arrows.

The linewidth of the main peak at 0.797 eV is 4 meV in our samples. As shown in the inset of Fig. 4 no hot lines could be resolved up to 85 K. Similar to the 0.943 eV emission also the strong 0.797 eV emission shows nearly no increase in linewidth and only the small shift of about 0.2 meV to lower energy.

On the low energy side of the 0.797 eV emission a broad shoulder appears. The maximum of this shoulder is close to the $E_2(\text{low})$ (30.7 meV) phonon mode, which is observed in Raman measurements. 76 meV lower in energy a further set of peaks appears. The spacing of the two main peaks at 0.722 eV (d') and 0.782 (c') agrees excellently with the $A_1(\text{TO})$ (76.1 meV) mode, which can be observed in Raman measurements.

In general the spectrum of the 0.797 eV luminescence center looks similar to the well-studied 0.84 eV emission of Cr in GaAs [12]. This luminescence center is attributed to an internal electronic transition of Cr^{2+} on a Ga substitutional lattice site. The tetrahedral environment of the Cr center is disturbed by a defect atom on one of the four As nearest neighbor sites. The 0.797 eV luminescence center may be caused by a similar defect. A 5T_2 ground state is a good possibility for this emission. Thus possible candidates are Mn^{3+} , Cr^{2+} , and V^+ .

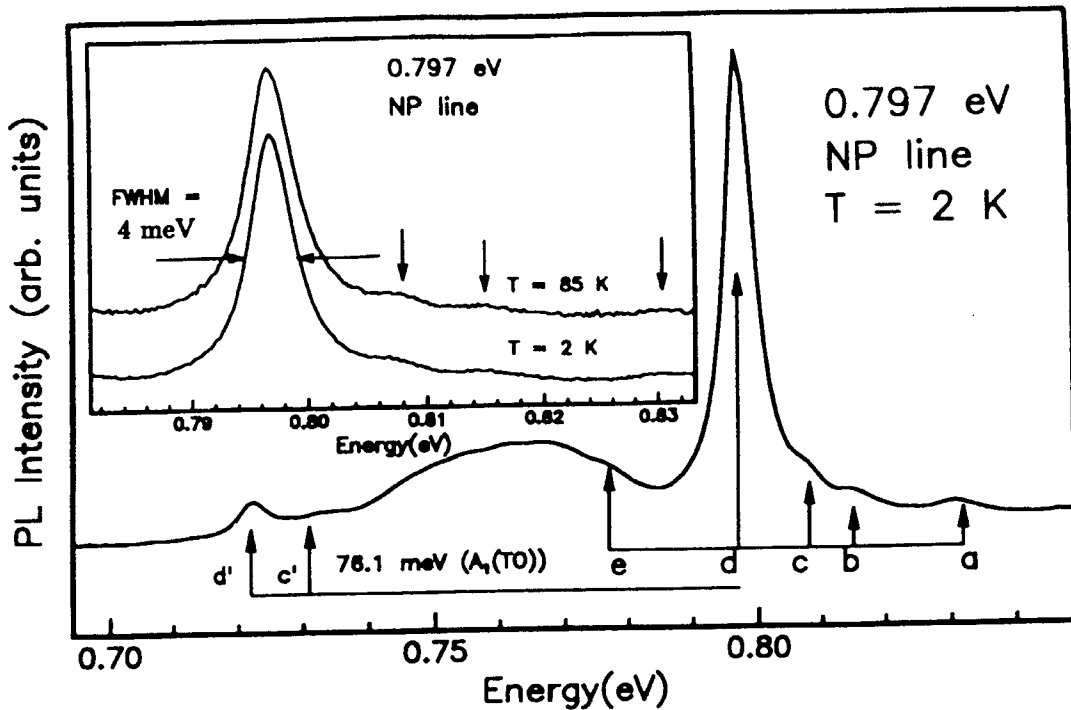


Fig. 4. PL spectrum of the 0.797 eV emission. In addition to the main no-phonon line we observe further weak satellite peaks indicated by the rake. The inset compares two spectra of the 0.797 eV emission detected at 2 K and 85 K.

To the 0.797 eV emission in AlN we also observed an emission with the main peak at 0.77 eV in GaN samples grown by the sandwich technique. This luminescence in GaN is shown in the upper part of Fig. 5. The shape looks similar to the 0.797 eV emission, but it is broader and therefore possible fine structures can not be resolved.

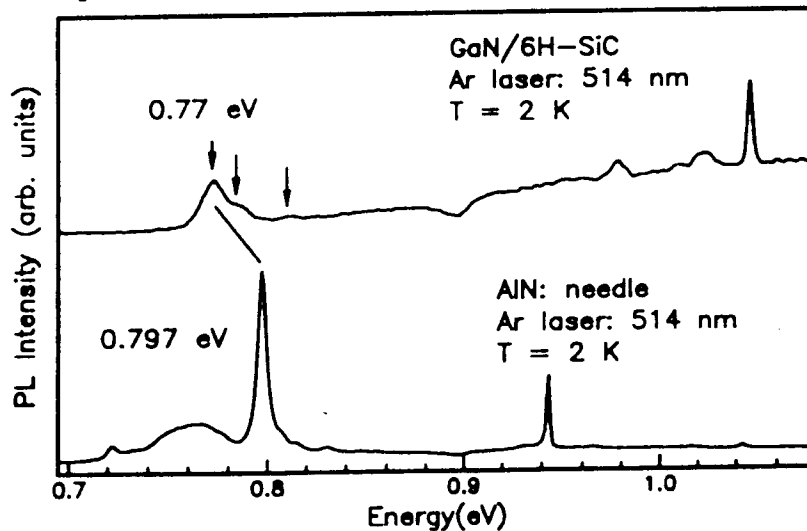


FIG. 5. PL spectra of AlN and GaN in the optical range of between 0.7 eV and 1.4 eV. The emission at 0.797 eV seems to have a counterpart in GaN at 0.77 eV.

CONCLUSIONS

By photoluminescence we studied residual transition metals in AlN. We observe three luminescence centers at 1.043 eV, 0.943 eV, and 0.797 eV. As already pointed out by Baur et al. [4] it seems possible to transfer the identifications of internal electronic transitions in GaN also to AlN. In Tab. I transition metal emissions in AlN and GaN are summarized.

AlN Energy (eV)	GaN Energy (eV)	possible identification in GaN
1.297 [2,3]	1.30 [2,3,5]	Fe ³⁺ (⁴ T ₁ → ⁶ A ₁)
1.201 [4]	1.193 [7]	Ti ²⁺ (¹ E → ³ A ₂)
1.043 this work	1.047 [11], this work	3d ⁷ (Co ²⁺ , Ni ³⁺)
0.943 this work	0.931 [4]	V ³⁺
0.797 this work	0.77 this work	transition metal complex

TABLE I. Comparison of transition metal emissions in AlN and GaN. The possible identifications obtained for GaN also seem to fit in AlN.

On the basis of a comparison with GaN the 1.043 eV center in AlN is caused by the same contaminant as the 1.047 eV emission in GaN. An exception to these nearly equivalent transition metal energies is the 0.943 eV emission in AlN. In contrast to the 0.931 eV emission in GaN the 0.943 eV emission in AlN shows no hot line. In general the intense 0.943 eV no-phonon line shows similar properties as the 1.19 eV emission in GaN. Thus it might also be attributed to a ¹E → ³A₂ transition. Possibly for V³⁺ in AlN the ¹E excited state shifts below the ³T₂ state as observed for Ti²⁺ in GaN [7]. The 0.797 eV no-phonon line has at least 4 weak satellite peaks. The whole spectra looks like the 0.84 eV luminescence of Cr in GaAs. Probably a similar transition metal complex is responsible for this emission. Zeeman measurements are now essential to identify these defects.

Reasons for the appearance of the internal electronic transitions at about the same energies in GaN and AlN are the same neighborhood of nitrogen atoms (N has a much larger electronegativity than P and As), the almost equal covalent bonding, the similar lattice constant, and the large bandgap.

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