

## Point Defect Content and Optical Transitions in Bulk Aluminum Nitride Crystals

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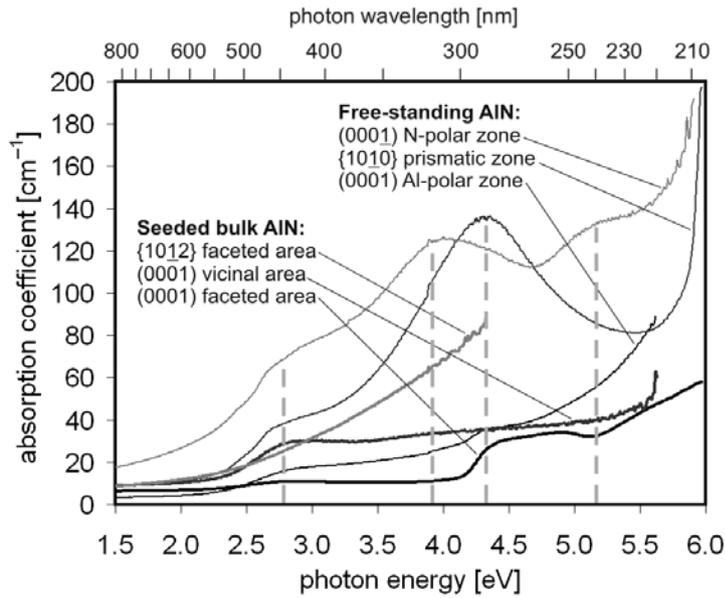
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In recent years, single-crystalline AlN gained interest as substrate material for epitaxy of group-III nitrides. Significant progress was made in wafer size, crystal quality, and yield using the physical vapor transport (PVT) technique to growth large-area aluminum nitride (AlN) bulk single crystals. A steep increase in quantum efficiency is observed in UV optoelectronic devices fabricated on low-defect bulk AlN substrates. On the other hand, even colorless AlN substrates show high optical absorption coefficients at wavelengths below 300 nm, which is clearly inadequate e.g. for deep-UV light emission through the substrate. The causative point defects are still not identified and their concentrations in bulk AlN, especially regarding intrinsic defects, are unknown. Especially the formation of vacancies ( $V_{Al}$ ,  $V_N$ ) and defect clusters is very difficult to evaluate experimentally. Such defects are predicted by first-principles calculations to form at very different concentrations depending on the Fermi level (i.e. on the presence of other defects). Finally, the usable set of growth parameters in PVT growth of AlN is restricted, and any attempt to adjust the residual point defect content in bulk AlN remains disputable. This presentation aims at evaluating the point defect content in nominally undoped bulk AlN crystals from optical absorption and luminescence measurements.

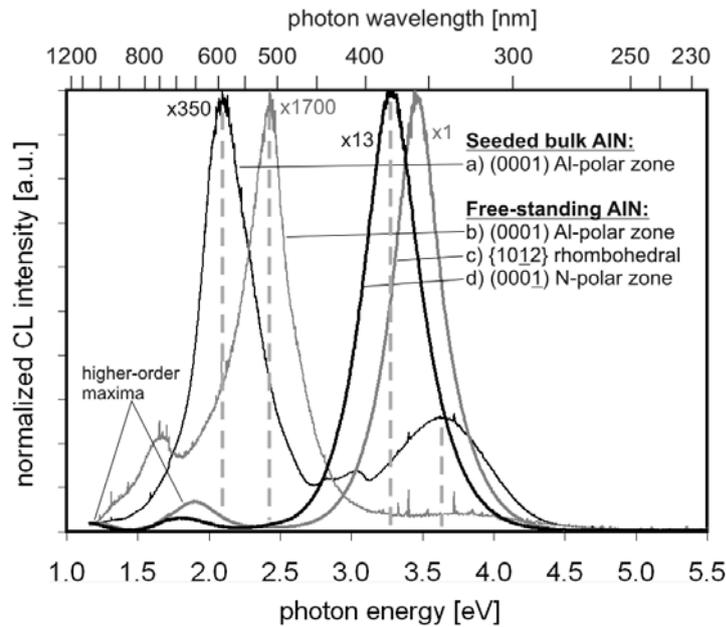
Bulk AlN crystals were grown by PVT, i.e. sublimation and recondensation of an AlN charge placed in a tungsten crucible, as reported earlier. Spontaneously nucleated free-standing crystals [1] as well as crystals seeded on AlN templates [2] were cut into wafers and polished on both faces. Oxygen content was about 100 ppm wt; all other impurities except carbon (and possibly hydrogen) are well below 2 ppm wt as evidenced by mass spectrometry and inert gas fusion. The crystals are typically faceted, thus growth takes place on differently faceted areas simultaneously. As a consequence, the crystals exhibit a zonal structure. Within a single crystal, different zones manifest itself most clearly in differences in optical absorption and luminescence spectra [1]. In both cases, broad below band-gap features are observed at room temperature that remain virtually unchanged in low-temperature measurements down to 8 K. In the following, we will refer to a zone by the crystallographic facet which formed the respective volume area.

Example spectra for optical absorption (OA) are presented in Fig. 1. Two major absorption bands are identified, one fixed at approx. 2.8 eV, and one shifting from 3.9 eV to 4.4 eV, as the zones go through from N-polar basal (000 $\bar{1}$ ) and prismatic {10 $\bar{1}$ 0} to Al-polar rhombohedral {10 $\bar{1}$ 2} and finally Al-polar basal (0001). The strength of the first band is anti-correlated to the shift towards higher energies of the second band. In N-polar (000 $\bar{1}$ ) zones, another band at around 5.2 eV is clearly identified (dashed lines in Fig. 1). Furthermore, the OA bands at 2.8 eV and at 5.2 eV clearly feature different polarization-dependent transitions [3]. Below band-gap cathodoluminescence (CL) spectra of different zones of bulk AlN are shown in Fig. 2. The spectra yield two very intense and partially overlapping bands in the range of 3.3–3.6 eV. The peak intensity decreases over orders of magnitude – and the maximum shifts to higher energies – as the zones go through from N-polar (000 $\bar{1}$ ) and prismatic {10 $\bar{1}$ 0} to rhombohedral {10 $\bar{1}$ 2} zones. These bands dominate all spectra except the ones taken on an Al-polar (0001) facet or zone. In the latter areas, CL is orders of magnitude weaker and dominated by a band in the 2.1–2.5 eV energy range. Additional bands are observed around 3.4–3.6 eV and in the 4.0–4.4 eV range (dashed lines in Fig. 2).

A per-sample comparison between OA and CL measurements is unfeasible as both methods provide a very different probing volume and area. However, we find that the CL intensity and shift in peak position of the main bands in the 3.3–3.6 eV energy range show the same dependency on zonal



**Fig. 1:** OA spectra of different zones in bulk AlN.



**Fig. 2:** Normalized CL spectra of different zones in bulk AlN.

N-polar grown samples. Finally, the 5.2 eV OA band may be attributed to oxygen or  $V_N$ , depending on the Fermi level and total oxygen content. Prismatic and rhombohedral samples lie in between; the strong, broad optical transitions are a superposition of transitions from  $V_{Al-O_N}$  and  $V_{Al}$ . In conclusion, the oxygen contamination in different zones of nominally undoped AlN increases in the order Al-polar (0001), rhombohedral {1012} and prismatic {1010}, N-polar (0001). In the same sequence, the 2.8 eV absorption and thus the yellowish coloration of the zones increases. The concentration of  $V_{Al}$  increases with rising Fermi level, i.e. with increasing oxygen content.

structure as the OA in the 3.9–4.4 eV range. The energy difference can be explained by absorption of phonons in the OA case. According to first principles calculations and literature reports of CL on thin AlN films, the bands are assigned to transitions between the conduction band (CB) (or an unknown shallow donor) and the deep levels  $V_{Al}^{2-/3-}$  and  $(V_{Al-O_N})^{2-/}$ , which are located approx. 2.5 eV and 2.1 eV above the valence band, respectively. The 2.8 eV OA band (which has no CL counterpart) is then attributed to a transition from  $V_{Al}^{2-/3-}$  to a deep acceptor 1.0 eV below the band-gap, which might well be the oxygen DX-center. This assignment is further supported by measurements of thermal activation energies.

Analyzing the strength of the optical transitions in different zones, we find that N-polar (0001) zones show strong optical transitions involving  $V_{Al}^{2-/3-}$  and oxygen. This indicates that the Fermi level is in the upper band-gap region, probably pinned to the oxygen level. In contrast, the Fermi level in Al-polar (0001) samples lies near mid-gap, in accordance to first principles calculations which predict that  $(V_{Al-O_N})^{2-/}$  is only stable if the Fermi level doesn't get close to the CB. This evidences a significantly lower oxygen content compared to

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- [3] M. Bickermann, A. Münch, B. M. Epelbaum, O. Filip, P. Heimann, S. Nagata, A. Winnacker, *J. Appl. Phys.* 103, 073522 (2008).