Growth and Characterization of AlN Bulk Crystals

Habilitationsschrift

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Abstract

In recent years, single-crystalline aluminum nitride (AlN) became a candidate as substrate material for group-III nitride epilayers. Devices based on such epilayers constitute a rapidly emerging market in the field of optoelectronics and high-frequency communications. Particularly UV optoelectronics would greatly benefit from the use of AlN substrates, if these were available in sufficient amount, quality, and size. That is still not the case. This thesis provides a review of the results and advances on growth and characterization of AlN bulk crystals that have been achieved at the University of Erlangen.

Bulk AlN crystals are most successfully grown by a sublimation–recondensation process (PVT growth) at temperatures exceeding 2000°C. A set-up based on tungsten parts was found to be most stable against the aggressive vapor and provides very low contamination of the growing crystal. We show that mass transport and unidirectional solidification may be easily established. However, grain selection and enlargement is very slow, as the crystals tend to form a columnar structure. Under nearly isothermal conditions, free-standing crystals of up to 25 mm in size and high structural quality have been fabricated. But further enlargement seems infeasible, and their special habit renders them unsuitable for preparation of substrates. Large-area AlN single crystals are obtained by seeding on SiC substrates, alas at the cost of severe problems in material compatibility which lead to highly contaminated AlN crystals. As the set-up degrades in the presence of SiC during long-time growth runs, the achievable crystal thickness is limited. Still, such large-area AlN crystals have been successfully used as templates for further growth of AlN single crystals up to 30 mm in diameter and 10 mm in height. In the main volume of such crystals, the density of dislocations threading the basal plane is lower than 10^5 cm^{-2}. However, low angle grain boundaries are inherited from the SiC seed and the template, leading to a mosaic structure of elongated subgrains which may deviate by more than 1° from the main orientation. Structural quality improves in crystals that were grown under optimized conditions. According to chemical analysis, oxygen is found to be the dominating impurity regardless of growth orientation. Additionally, silicon and carbon are clearly detectable even in bulk AlN grown homoepitaxially on the templates.

The wurtzite structure of AlN is highly anisotropic. As growth takes place on different facets simultaneously, the resulting crystal shows a zonal structure. Different zones of AlN single crystals showed very similar threading dislocation densities and topographies. On the other hand, impurity incorpora-

tion and formation of intrinsic defects clearly depends on the zone or growth orientation. The differences are evidenced by optical absorption and cathodoluminescence. It will be shown that both intensity and peak position of UV optical absorption are closely linked to the 'violet luminescence' in the 3–4 eV energy range. Comparing our data with experimental results and first principles calculations reported in literature, we establish a model of the defect content in nominally undoped AlN crystals. As a conclusion, oxygen contamination as well as aluminum vacancy formation increases in the order Al-polar (0001) zone, rhombohedral {10$\underline{1}$2} zones, prismatic {10$\underline{1}$0} zones, N-polar (000$\underline{1}$) zone. In the same sequence, the absorption at 2.8 eV and thus the yellowish coloration of the crystal areas increases. The model further suggests a DX-center formation of oxygen, whose thermal activation energy of 0.6–0.8 eV is evidenced by thermally stimulated luminescence and high-temperature resistivity measurements. In contrast, the existence of nitrogen vacancies in significant concentrations is disputed at least for samples in which the oxygen content governs the electrical behavior.

In conclusion, a procedure for homoepitaxial growth of AlN bulk crystals is developed. The structural quality of the resulting substrates is very promising for group-III nitride epitaxy. Additionally, important insights into the defect occurrence and distribution in this novel material are obtained, which may aid in further optimization of crystal growth in regard to applicability e.g. in UV optoelectronics. Finally, open issues in growth and characterization of AlN bulk crystals are discussed, and further ways of proceeding are suggested.

Contents