Growth of High Quality AlN Single Crystals and Their Optical Properties

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Abstract. Growth and optical properties of high quality AlN single crystals grown by physical vapor transport using powder sublimation is presented. Crystallinity, incorporated impurities and their effects on the optical properties are evaluated for different crucible materials and growth environments. A significant reduction of impurity incorporation was achieved using a two-step growth process in a TaN crucible. Crystal defects and the effect of incorporated impurities on the optical properties have been analyzed by their characteristic photoluminescence and absorption, Raman- and glow discharge mass spectroscopy.

The application of AlN bulk crystals as substrates in the group III-Nitride device fabrication process is expected to yield substantially reduced dislocation densities (below $1000/cm^2$) by minimizing the defects from the substrate and by reducing the lattice and thermal mismatch [1,2,3]. Hence, the growth and crystal quality optimization of bulk AlN crystals is of primary importance for the development of lattice-matched wafers for the fabrication of III-N based devices with improved characteristics and extended lifetime. In this paper, the growth of large, high-quality AlN single crystals is reported. Using different process conditions, the levels of contaminations and native defects were varied. The impact on the optical and crystalline quality of AlN was studied by absorption, luminescence, and Raman spectroscopy.

A physical vapor transport (PVT) process was used to grow bulk AlN crystals by sublimation of AlN powder in an ultra-high purity (UHP) nitrogen ambient. Employing the sandwich-sublimation configuration, the bulk crystal growth takes place in a reaction crucible, at growth temperatures of 1800-2400 °C, and pressures of 400-600 Torr. A resistively heated and an inductively heated reactor were used for the growth. The AlN powder sublimed from the bottom of the crucible, which was kept at a relatively

higher temperature with respect to the seed, forming gaseous species of Al and N_2. These species were then transported through the vapor phase to the top of the crucible where the crystal grew by re-crystallization at a relatively lower temperature. Three samples, labeled A, B, and C, grown at different temperatures, by different reactions procedures and in different crucibles were chosen for further investigations. The samples A and B were grown using a two-stage process, where the temperatures was gradually ramped between the two stages. Sample C was sliced from a cross section of a large-grain polycrystalline boule. A detailed description of the growth processes is reported in [4,5,6]. The exact crystalline orientation and quality were confirmed by Raman spectroscopy using the 632.8 nm line of a HeNe laser in backscattering geometry (not shown here). The E_2(low) mode at 246 cm^{-1}, the A_1(TO) mode at 609 cm^{-1}, the E_2(high) mode at 655 cm^{-1}, the E_1(TO) mode at 668 cm^{-1}, and the E_1(LO) mode at 911 cm^{-1} were revealed. The mode energies are in good agreement with the absorption bands in the FIR published for unstrained AlN [7]. Photoluminescence (PL) spectra of the AlN single crystals excited below and above the bandgap are shown in Fig 1. Broad luminescence bands with two maxima ranging between ~3.5 eV and 4.4 eV were observed in the spectra. Significant differences

in the intensities of the PL emission bands, strongly depending on the excitation energy, were detected. For below-bandgap-excitation, the emission maximum was found to be redshifted in comparison to the emission maximum found for band-to-band excitation in samples A and B, while only a small difference was found in the sample C.
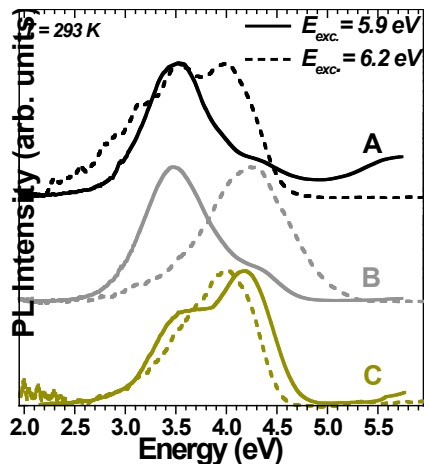

FIGURE 1. Photoluminescence excited below and above (dashed line) the bandgap of AlN single crystals recorded at room temperature.

Despite the fact that the PL maximum was most redshifted for the sample with the highest oxygen contamination (#B), when excited below the bandgap energy, the PL emission maximum ranged between 3.9 eV and 4.3 eV for band-to-band excitation. In the latter case, peak energy of sample B was found to have the highest transition energy. The peaks above 4 eV have been in absorption, but not in PL assigned to oxygen related defects. In PL, emission peaks around 3.5 eV are attributed to oxygen related impurities [8]. Harris and Youngman [8] found that with increasing oxygen concentration the emission peak energy shifts to lower energies. In our experiments, this behavior was confirmed for below bandgap excitation. According to their excitation behavior the bands at ~3.5 eV were tentatively assigned to transitions between a deep impurity center and the valence band. The comparison of the obtained PL and absorption spectra with the elemental analysis data (e.g., oxygen concentrations varying from 50 ppm in sample C up to 1200 ppm in sample B) rules out that oxygen alone is generating the emission band around 3.5 eV. No correlation of this emission band with the oxygen contamination level was detected. Applying band-to-band excitation, sample B with the highest concentration of oxygen exhibited the weakest emission at ~3.5 eV. In addition, the absorption coefficients (not shown here) in the whole UV range were found to be smallest in the sample B, where one

would expect a strong absorption around 4.3 eV for oxygen related defects. Hence, other impurities or defect centers need to be considered as possible culprits for these transitions. Glow discharge mass spectroscopy revealed that in addition to O, Si and C were present in the crystals at concentrations that may have a significant influence on the luminescence properties of AlN. In carbon-doped AlN films, C or C-related defect complexes may cause impurity states with respective transition energies around 4.4 eV [9]. However, in this study no obvious correlation was detected between the C concentration and the dominance of this PL peak.

In summary, high quality AlN single crystals were obtained by a physical vapor transport process. Varying levels of oxygen, silicon, boron and carbon contaminations were detected. Optical and mass spectroscopy suggest that oxygen is only one of contaminants having a strong impact on the optical properties of bulk AlN.

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