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Strongly enhanced deep UV transparency of AlN bulk crystals grown by physical vapor transport

C. Hartmann, J. Wollweber, A. Dittmar, F. Langhans, S. Kollowa, K. Irmscher, M. Bickermann

Bulk AlN crystals with high structural quality are considered as the most promising substrate material for UVC LEDs based on $Al_xGa_{1-x}N$ layers with high Al content. Efficient UVC LEDs are ideally suited for water disinfection, biological agent detection, and medical diagnostics. In order to exploit the potential of AlN substrates they should be deep UV transparent since the light is extracted through the AlN substrate in the current UV LED layouts. Absorption coefficients at the emission wavelength (250 - 280 nm) of $\alpha < 15$ cm^{-1} are highly desirable.

Bulk AlN crystals are grown by physical vapor transport (PVT) at temperatures exceeding 2000°C. Impurities such as oxygen, carbon, and silicon as well as compensating intrinsic defects lead to optical transitions within the wide band-gap of about 6.0 eV. Strong absorption around 4.7 eV (265 nm) is caused by carbon related defects[1,2]. This absorption can be quenched for [O] >> [C], probably due to the shift of the Fermi level which results in a change of the charge state of the carbon related defects. Furthermore, significant absorption tailing off from the band edge into the UV range of interest is presumably caused by oxygen. We will show that the concentrations of the main impurities in the crystals must fulfil the following conditions in order to achieve the required low UV absorption ($\alpha_{265\,nm} < 15$ cm^{-1}):

$$[O] > 3\,[C] \qquad (1)$$

$$[C] + [O] < 10^{19}\ cm^{-3} \qquad (2)$$

These conditions can be achieved for the PVT growth of AlN single crystals on the N-polar facet at seed temperatures T_{Seed} ~ 2040 °C using getter materials for oxygen and carbon. Adding coarse-grained TaC material on the top of the AlN source has proven to be highly efficient by converting $Al_2O(g)$ to CO(g) by the following reaction:

$$2TaC + Al_2O(g) + N_2(g) \rightarrow Ta_2C + CO(g)\uparrow + 2AlN \qquad (3)$$

CO(g) is stable under growth conditions and will be gradually removed from the crucible by dilution with the N_2 ambient gas. Remaining volatile carbon can be efficiently gettered by adding tungsten sheets inside the TaC crucible which reacts partially to W_2C during the growth:

$$2W + C \rightarrow W_2C \qquad (4)$$

A progressive reaction from W_2C to WC by

$$W_2C + C \rightarrow 2WC \qquad (5)$$

must be prevented as it decreases the getter effect drastically due to the high carbon activity at growth conditions in case of [W] < 2[C]. Best values of $\alpha_{265\,nm} = 14$ cm^{-1} are achieved at [O] = $6.4\times10^{18} cm^{-3}$ and [C] = $1.8\times10^{18} cm^{-3}$ which fulfills the conditions of eq. (1) and (2). Entire AlN wafers (Ø ≥ 10 mm) with $\alpha_{265\,nm}$ = 25-28 cm^{-1} can be grown in a reproducible manner.

The combination of the high deep UV transparency with the high structural quality of the grown AlN crystals grown by our PVT growth technology[3] (no low-angle grain boundaries, rocking curve FWHM = 11-18 arcsec) will provide all requirements necessary for the preparation of highly efficient $Al_xGa_{1-x}N$ UVC LEDs on AlN substrate wafers.

1 R. Collazo et al., *Appl. Phys. Lett.*, 2012, **100**, 191914.
2 K. Irmscher et al., *J. Appl. Phys.*, 2013, **114**, 123505.
3 C. Hartmann et al., *CrystEngComm*, 2016, accepted manuscript, *DOI: 10.1039/C6CE00622A*.

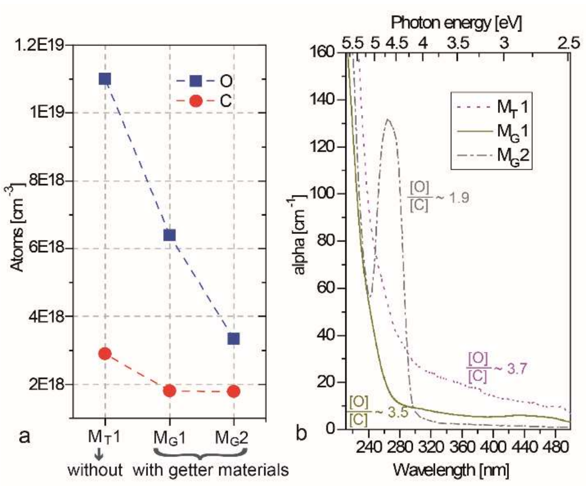

Fig. 1:(a) Carbon and oxygen concentrations and (b) absorption spectra in dependence of the use of the getter materials TaC and W. For the measurement spots M_T1 (crystal grown without getter materials) and M_G1 (with getter materials) the [O] > 3 [C] condition (eq. 1) is fulfilled and the 265 nm absorption band is absent. M_G1 additionally meets [C] + [O] < 10^{19} cm^{-3} (eq. 2) resulting in $\alpha_{265\ nm}$ = 14 cm^{-1}. M_G2 shows the lowest overall total impurity concentration, but despite the low carbon concentration, the 265 nm absorption band shows up because eq.1 is not met, resulting in $\alpha_{265\ nm}$ > 100 cm^{-1}.

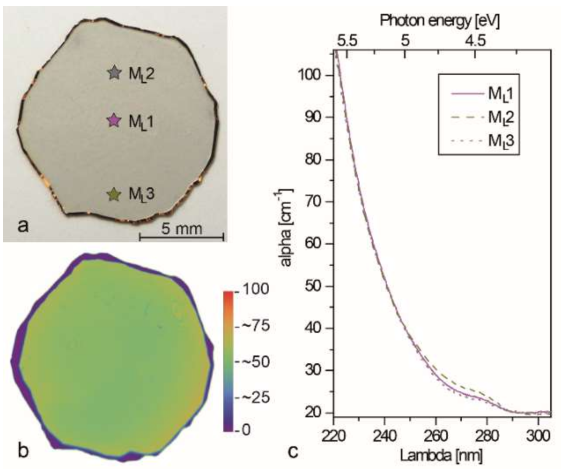

Fig. 2: (a) Optical image of a c-plane AlN wafer (Ø ~11 mm) with measuring spots; (b) transmittance of this wafer at 254 nm (wafer thickness = 140 µm); (c) absorption spectra at the measuring spots. Except for the outermost rim, the entire AlN wafer shows $\alpha_{265\ nm}$ = 25-28 cm^{-1}

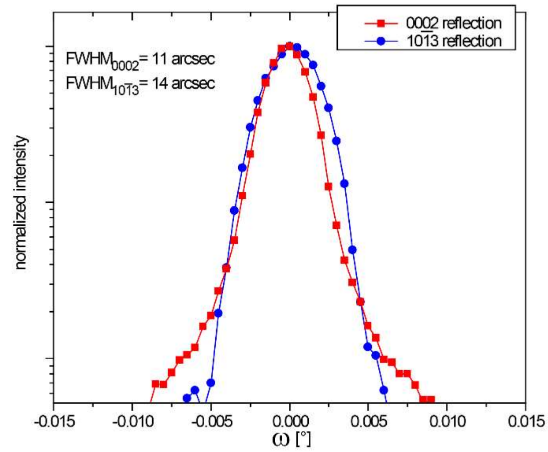

Fig. 3: Rocking curves (semi-logarithmic scale) measured with 4-bounce Ge-220 monochromator and open detector aperture over the full as-grown (000-1) facet area of a typical AlN crystal in the 0002 and 10-13 reflections