AlN bandgap temperature dependence from its optical properties

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ABSTRACT

In the present work we report on the AlN gap energy temperature dependence studied through the optical properties of high-quality large bulk AlN single crystals grown by a sublimation–recondensation technique. The cathodoluminescence, transmission/absorption as well as optical reflectance measurements at low temperature show a clear feature at about 6.03 eV, which could be attributed to the free exciton A. Even using a rather thick sample it was possible to observe the absorption due to the free exciton A in this energy range due to its large binding energy. We followed the temperature evolution of these features up to room temperature and inferred the gap energy temperature dependence using the exciton binding energy obtained by our group in the past.

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1. Introduction

The rapid research progress of the III-nitrides in recent years culminated with the commercial availability of a number of optoelectronic devices. Reductions in the dislocation density have resulted in improved electron mobility in AlN as well as the fabrication of PIN homojunction light emitting diodes (LEDs) with emission as low as 210 nm [1]. This layered structure device was grown on a SiC (0 0 0 1) substrate. In order to cover the whole deep UV region, high-quality $Al_xGa_{1-x}N$ alloys with high Al mole fractions are required. A homoepitaxial film could improve the already high-quality $Al_xGa_{1-x}N$ alloy layers in these devices, consequently allowing the improvement of quantum efficiency and delivered power. Despite the success in obtaining short wavelength emission for such devices, the achieved external quantum efficiency of the order of 10^{-6} is still considered very low. Therefore, high-quality AlN substrate is a key factor in the attempt to improve deviced quality layers with high Al mole fraction, since it would be chemically compatible with the substrate, would minimize the stress built up inside the film, allowing for the growth of thicker film layers, be able to dissipate the heat much more efficiently during operation and avoid the problems caused by differences in the thermal expansion coefficients.

Optical characterization methods provide unique access to intrinsic and extrinsic material properties. Studies on the near band-edge optical properties of AlN have been restricted to only a few research groups due to technical difficulties involved in the deep UV optical measurements and the lack of high-quality AlN crystals. As an example, only a small number of publications have reported the detection of emission of AlN. The majority of the studies discussed the photo- and cathodoluminescence (CL) and reflectance (OR) characterization of AlN films [2–12], and fewer focused on bulk AlN single crystals [13–15].

Wurzite-type AlN presents three valence bands at the Γ point of the Brillouin zone as a result of the noncubic crystal-field and spin–orbit splittings lifting the degeneracy of the p-like valence bands. Nonetheless, the AlN band structure and even its gap energy value are still a matter of ongoing discussion in the literature. Photoluminescence spectroscopy combined with first-principles band structure calculations have shown that the discrepancy in band-gap values for the AlN found in the literature could, in part, be lifted in terms of selection rules for the optical transitions [5]. Further experimental investigations corroborated with the previous statements [14,15]. CL and OR revealed the AlN excitonic structure, allowing the estimation of the spin–orbit and crystal-field splittings [14].

In the present work, we report on the optical properties of high-quality large bulk AlN single crystals grown by a sublimation–recondensation technique. Diverse single-crystal wafers of AlN, obtained by cutting and polishing the crystals from the former growth step, were investigated using CL, transmission/absorption and OR measurements at different temperatures.

2. Experimental details

The high-quality large bulk AlN single crystals used here were grown by a self-seeded sublimation–recondensation technique [16]. The crystalline quality of the samples has been tested by X-ray diffraction measurements. More details on growth and structural characterization can be found elsewhere [16,17]. For

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the CL measurements, a commercial electron gun, installed in an ultra high vacuum chamber, was used to excite the samples at different excitation densities. Electron beam (e-beam) currents between 1 and 5 μA and e-beam energies between 5 and 15 keV were typically used. The spot size was determined to be approximately 80 μm. The energy density was kept between 40 and 1000 W/cm². After exciting the AlN samples, the light emitted by the samples was collected and focused by a set of parabolic mirrors with matching numerical apertures, and dispersed by a double spectrometer fit with 1200 grooves/mm gratings. The dispersed light was subsequently detected by an UV-sensitive GaAs photomultiplier connected to a computer-controlled photon-counter. Inside the vacuum chamber the samples were mounted on a cold finger cryostat with a controlled temperature varying from 5 to 300 K. For the absorption and OR measurements, the light from a 150 W deuterium lamp dispersed by a 0.5 m monochromator, equipped with a 1200 groves/mm grating, was used as the light source. After interaction with the sample the light was detected by a solar-blind photomultiplier attached to a photon-counter system. The whole light path had been purged and kept with nitrogen gas overpressure in order to minimize absorption by the oxygen molecules present in the air.

3. Results and discussion

Fig. 1 shows typical spectra of AlN samples obtained from CL, OR and transmission (trans.) experiments in the near band-edge energy range at 6 K for CL and OR and 7.5 K temperature for the transmission experiment. The CL spectrum has been measured using 5 keV as the e-beam energy and 5 μA as its current. This spectrum shows five different transitions, which have been tentatively assigned to free and bound exciton recombination processes based on temperature quenching studies [18]. In this spectrum the A-exciton is at approximately 6.03 eV as a shoulder of the most intense line at 6.010 eV attributed to a neutral donor-bound-exciton recombination. Reflectance measurements supported in part the assignments presented in the previous work, where the so-called A-exciton could be observed in the same energy range [14], as depicted in the OR spectrum in Fig. 1. The representative OR spectrum, taken from an a-faced AlN-crystal wafer, shows a typical excitonic transition line shape over the same energy range as the line observed in the CL data. Also in

Fig. 1 a typical near-band-edge transmission curve, named trans., for our AlN sample is shown in its upper part. The pronounced valley along the transmission edge is also attributed to the A-exciton, since it occurs in the same energy as the transitions observed in the OR and CL data, although measured in a slightly different temperature. This assignment will be discussed later in this text. Following this we studied the temperature evolution for all the spectra shown in Fig. 1. For the CL measurements a temperature evolution can be found elsewhere [18,19].

Fig. 2 depicts the temperature evolution of the OR spectra from 6 up to 294 K for the AlN bulk sample. It is possible to observe a decrease in the energy of the transition as the temperature increases. The asymmetric line shape due to the excitonic transitions in the reflectivity data has been fitted to a Lorentzian dielectric function, assuming the same number of oscillators at all temperatures. A more detailed discussion of the procedure can be found elsewhere [14]. These results, together with the results for the CL measurements, are summarized in Fig. 4.

Fig. 3 shows typical near-band-edge absorption curves of an AlN-single crystal taken at different temperatures from 7 up to 300 K. Even though the sample was about 120 μm, a pronounced shoulder along the absorption edge could be observed. This shoulder is attributed to the so-called A-exciton, and its observation was only possible due to the large binding energy of approximately 63 meV [19], which makes it to show itself detached from the absorption edge. In order to rule out any artifact causing the observed feature in the absorption spectra we conducted a series of experiments tuning the detector efficiency curve. By using different absorption filters between the sample and the detector itself, i.e, after light reaching on the sample surface, we could exclude the possibility of any defect luminescence band instead of the actual absorption due to the near-band-edge energy range.

The energy gap in semiconductors in general changes due to contributions from the electron–phonon interaction and due to the lattice thermal expansion [20–23], the former being the most important in the process. There are several models describing the energy gap as a function of temperature for a semiconductor. Some of them are empirical, in the sense that they describe the experimental data without offering a physical meaning for the parameters involved, as in the Varshni model [24]. Other semi-empirical models, involving for example Bose–Einstein statistics, could make a better description of the gap energy temperature
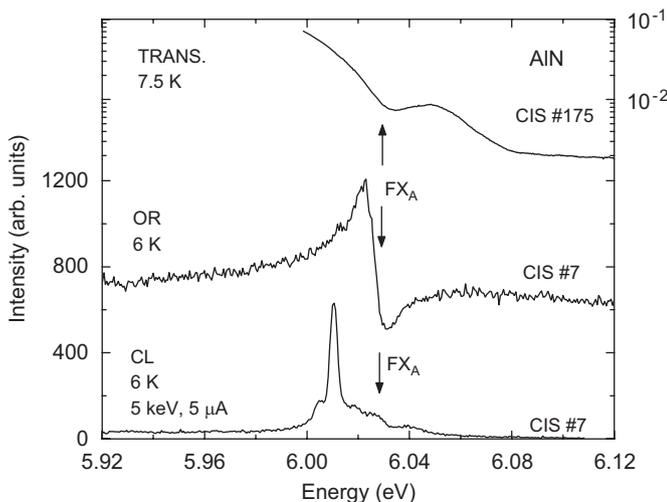

Fig. 1. Low-temperature cathodoluminescence (CL), optical reflectivity (OR) and transmission (trans.) spectra of AlN bulk crystals in the near-band-edge energy range. FX$_A$ indicates the position of the free exciton-A.
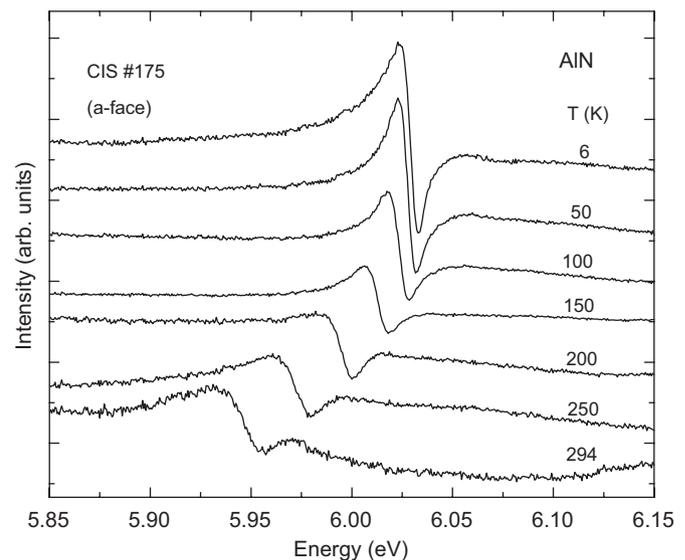

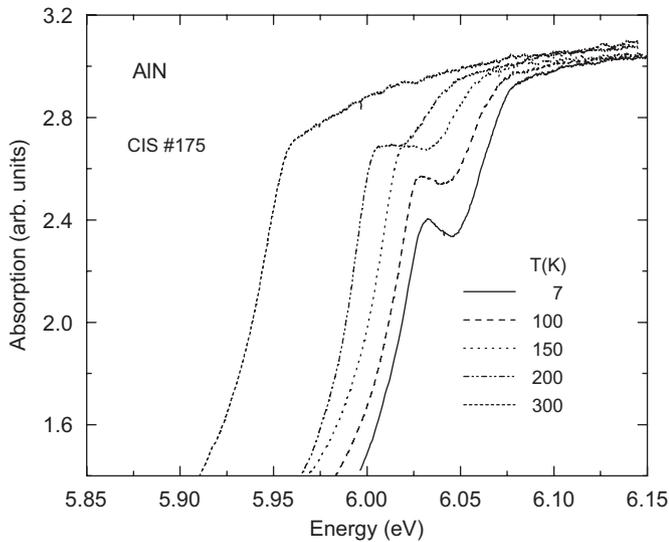**Fig. 2.** AlN optical reflectivity spectra as a function of temperature.

Fig. 3. AlN optical absorption spectra in the absorption edge energy range as a function of temperature.

Fig. 4. Energy positions of the A-exciton as a function of temperature. The hollow symbols represent the data obtained from the CL measurements for different AlN bulk crystals, the fully inverted triangles show the results from the OR experiments and the stars represent the results from the absorption experiments. The full line is a fit using a semi-empirical model [18] and the dashed line represents the gap energy evolution taking the A-exciton binding energy into account.

Table 1
Temperature coefficients for the AlN band-gap energy

Temperature coefficient (meV/K)	Substrate	Growth technique	Reference
0.51	6H-SiC	MOCVD	[11]
0.51	Sapphire	MOCVD	[11]
0.35	6H-SiC	LP-MOVPE	[2]
0.55	Sapphire	LP-MOVPE	[3]
0.45	Bulk	Sublim.–recond.	[3]
0.60	Sapphire	MOCVD	[24]
0.58	Bulk	Sublim.–recond.	This work

dependence [25,26]. The model proposed by Pässler et al. [26] contributed to understand the origins of some of the parameters used in previous semi-empirical models like the one proposed by Viña et al. [25]. More details are found elsewhere [27–32].

Fig. 4 summarizes the temperature dependence of the free exciton A line positions obtained in the experiments discussed above. In this figure the hollow symbols represent the data obtained from the CL measurements for different AlN bulk crystals, the fully inverted triangles show the results from the OR experiments, depicted in Fig. 2, and the stars represent the results from the absorption experiments. One can observe the same temperature behavior for all groups of data from the different experiments, with an almost constant energy value in the low-temperature range, decreasing in energy for higher temperatures. The curve used to describe the temperature behavior of the AlN energy gap (full line in Fig. 4) represents a fit using the Pässler model [26]. Although this model involves Bose–Einstein statistics and spectral functions to describe the electron–phonon interaction, it still depends on experimental parameters. It is therefore not possible to find the right curve parameters without the adjustment of the parameters based on experimental data. Nonetheless, this fit is in very good agreement with the experimental data as one can see from the figure. By taking into account the A-exciton binding energy obtained by us previously [19], it is possible to estimate the evolution of the AlN gap energy as a function of temperature. The dashed line in Fig. 4 represents the estimated AlN gap energy as a function of temperature. Extrapolating the gap energy value for very low temperature we estimate the AlN gap to be approximately 6.09 eV, reaching 6.00 eV at room temperature.

One common characteristic for the experimental data on the AlN energy gap as a function of temperature found in the literature is its almost linear behavior for temperatures above approximately 200 K up to room temperature. This is an important parameter for the development of optoelectronic devices working at room temperature, since it will influence, for example, the emission wavelength of such devices. Some of the temperature coefficients for the band-gap energy of AlN for temperatures above 200 K described in the literature are shown in Table 1. As one can see from this table, our results compare very well with the ones obtained from bulk samples grown on sapphire substrates [11,3,33]. The fluctuation observed in result from Ref.
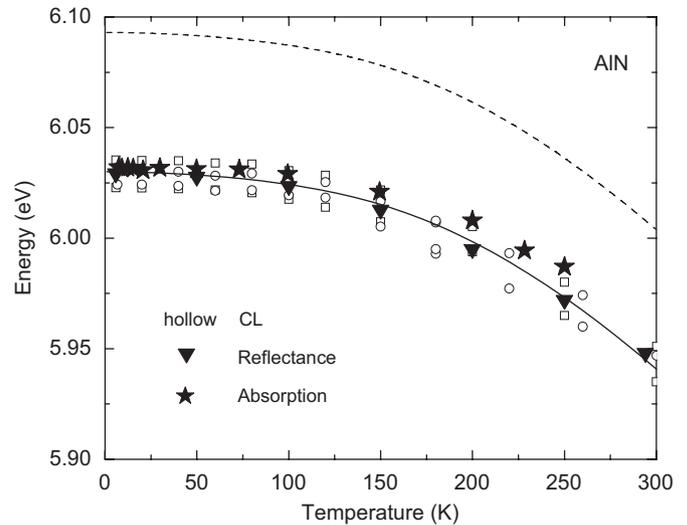
[2] may be attributed to strain fluctuations and even different sample temperatures. A direct comparison between our results and the ones published before is not possible at this point, since it lacks on a common figure of merit for the sample quality.

4. Conclusions

The optical properties of AlN bulk crystals have been investigated using cathodoluminescence, optical reflectance and transmission/absorption experiments. The temperature dependence of the structures assigned to the AlN A-exciton shows a very good agreement among the results from the three experimental optical techniques. The energy positions of the A-exciton line were fitted using a semi-empirical model proposed by Pässler et al. [26], which we found to be the best one to describe it. Using the binding energy for the A-exciton we proposed the gap to be at approximately 6.09 eV for low temperature and at 6.00 eV for room temperature.

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