Luminescence properties of AlN nanostructures revealed under UV light irradiation

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Abstract. The luminescence properties of the AlN nanostructures – nanorods and nanotips - revealed under the UV irradiation are similar to those of the AlN ceramics. Presumably they are induced by the recombination processes in the oxygen-related centers. All the studied luminescence processes (photoluminescence, thermoluminescence and optically stimulated luminescence) in the nanostructures occur mainly through the host lattice excitation. That may be explained by the smaller concentration of the defect centers and more perfect structure of the host lattice of the nanostructures compared to the ceramics. The small mutual differences revealed in the spectra and TL curves of the AlN nanotips and nanorods possibly arise due to the modifications of the host lattice structure and variations of the defect concentration during production of the samples.

1. Introduction

AlN is a wide band (6.2 eV) material potentially prospective for numerous practical applications in microelectronics and optoelectronics. Luminescence properties of the bulk AlN material have been studied rather well. A typical luminescence spectrum in the visible region comprises bands around 400, 480, and 600 nm [1-3]. These bands are assigned to recombination luminescence with participation of the defect centers, mainly oxygen-related. Oxygen is the natural dopant of AlN, substituting for nitrogen in the lattice. Apart from these, the high purity AlN samples reveal the near-edge emission bands (around 206 nm) due to the exciton luminescence [4-5]. In our works [6-7] we have studied also the processes of the light sum storage and release in AlN ceramics revealed by the methods of thermoluminescence (TL) and optically stimulated luminescence (OSL) and came to the conclusion that these processes are also determined by oxygen impurities in the AlN lattice because the TL and OSL emission spectra contain the same emission bands as the photoluminescence (PL).

Recently different types of AlN nanosize structures have been produced with different methods arousing an interest about the luminescence processes in these materials [8-11]. Emission spectra of these nanosize AlN materials have different composition depending on the structure type, size and synthesis method, but most of them contain emission bands around 400 and 600 nm apart from others. The given work is dedicated to the studies of the luminescence properties of the AlN nanostructures – nanorods and nanotips and their comparison with those of AlN ceramics obtained under the similar experimental conditions.
2. Experimental

Both AlN nanorods and nanotips have a form of a thin layer of AlN nanostructures grown on a silicium substrate. They were produced in National Taiwan University by thermal CVD method in the NH\textsubscript{3} atmosphere at 900-1100 °C [12]. The difference is in the shape of the structures: nanotips have a form of cones with the monotonously decreasing diameter along the length, while nanorods are prisms with a constant diameter. The height of structures is around a micron. The thickness of nanorods is around hundred nm, the thickness or nanotips decreases from hundred nm at the bottom to about ten nm at the top.

AlN ceramics were produced in the Institute of Inorganic Chemistry in Latvia, sintering in the vacuum fine powders of AlN and Y\textsubscript{2}O\textsubscript{3} (sintering aid - 5 wt.%) at 1700 °C during 300 min. Ceramics grain size was estimated to be in the 2-5 μm range. The produced ceramic cylinders were cut into 1 mm thick platelets.

The luminescence measurements were carried out in the Institute of Solid State Physics, Latvia, using the experimental setup described elsewhere [7]. The PL, OSL measurements and irradiation for TL were fulfilled at room temperature. The TL measurements were done inserting the samples into the self-made holder with the small heating device providing a linear heating with the rate 2 °C/sec. The sample holder was placed in the setup for spectral measurements. A red laser light (650 nm, 40 mW) was used for the OSL stimulation. All the spectra given in the paper are corrected for the instrumental response, except those on Fig.5.

3. Results

Luminescence properties revealed under the irradiation with UV light were studied for AlN samples of different types: ceramics, nanorods and nanotips, using the methods of PL, TL and OSL.

3.1. Photoluminescence. Under the UV irradiation the AlN ceramics show a strong PL signal with the main emission bands around 390, 480 and 600 nm (Fig.1.) All these bands can be excited in the host lattice absorption region (200-210 nm), and besides each of them has its own excitation band: the 390 nm and 480 emission bands are excited in the 240 nm and 290 excitation bands, correspondingly (Fig. 2, curves 1, 2), but the 600 nm emission band has a number of excitation bands in the 240-400 nm range (not shown in figures). All these excitation bands located in the 220-400 nm spectral range are due to the absorption of the defect centers.

![Fig.1. PL spectrum of AlN ceramics.](image-url)
PL emission spectrum of AlN nanostructures is similar to that of AlN ceramics: it contains a short wavelength band at about 380 nm, and bands at 480 and 600-700 nm. The short wavelength band is obviously complex, consisting at least from two subbands, with peaks around 360 and 420 nm. From the Fig. 3, it is seen that the relative contribution of the emission bands of both types of samples depends upon the excitation wavelength.
The spectra of the PL excitation (Fig.4) show that the PL of the nanostructures is excited mainly in the host lattice absorption region (195-210 nm) and slightly in the defect absorption region at 220-230 nm (380 nm emission band) and at 260 nm (480 nm emission band). Unlike the ceramics where excitation is observed in the 200 - 400 nm range, nanostructures have the PL excitation spectrum concentrated in the 200 – 300 nm region with a dominant near-edge part. From Fig. 3 and 4, it is seen that spectra of both nanostructure samples are very similar, except for the particularly strong excitation of the short wavelength band in the 195-210 nm region in the case of the nanorods.

3.2. Thermoluminescence. It was found that the TL is observed after exposure to UV irradiation in all the studied AlN samples. In AlN ceramics the TL response is very strong, making this material interesting for potential application in UV dosimetry. The TL emission spectrum contains the 400, 480 and 600 nm bands [13]. However the 600 nm band is overlapping with the glow spectrum of the oven, that's why usually it is not detected. The main interest is devoted to the 400 and 480 nm bands.

The TL excitation spectrum of AlN ceramics was measured separately for each of these TL emission bands and shown in Fig. 2, by curves 5 and 6. The separation of the curves of the TL excitation spectrum is not as distinctive as in the case of the PL excitation, but still it is clearly seen that they are mutually shifted; the TL excited below 270 nm contains mainly the 400 nm emission band, while excitation above 270 nm produces the TL signal where the 480 nm band is dominant.

The TL response of AlN nanostructures is much lower than that of AlN ceramics. Irradiation wavelengths were selected using the interference filters. The TL excitation spectra of the nanostructures shown in Fig.5 by curves 1 and 2, are obtained as the integral TL signal at 380 nm versus wavelength of the interference filter transmission peak. Similar curves were obtained for the 480 nm emission (not shown in the graph). From this figure it is seen that in the case of nanorods TL is excited mainly in the 200-220 nm region, while the TL excitation curve for the nanotips forms a band with the maximum about 230 nm.

The TL curves for all types of the AlN samples are shown in Fig.6. In the case of the ceramics the shape of the TL curves depend on the emission and excitation wavelength. Notwithstanding the overlapping of the TL emission bands and excitation regions it is seen that excitation in the 240 nm absorption band produces the TL with the dominant 400 nm emission band, which is connected with the low temperature TL peak at 70 ºC, while excitation in the 290 nm absorption band produces TL with the dominant 480 nm emission band and corresponding high temperature TL peak at 210 ºC.

For both nanostructure samples the shape of the TL curves does not depend on the selected emission and irradiation wavelength. In all cases the TL peak is situated around 80 ºC for nanorods and around 100 ºC for nanotips.
Fig. 5. TL (1, 2) and OSL (3, 4) excitation spectra of the nanorods (1, 3) and nanotips (2, 4). In all cases the 380 nm emission was selected. The curves are not corrected for the UV source lamp spectral distribution.

Fig. 6. TL curves of AlN ceramics and nanostructures. Wavelengths of emission and excitation are marked on the graphs.
3.3. *Optically stimulated luminescence*. The UV light induced OSL was observed in all the studied AlN samples under stimulation with the red light. Their OSL emission spectra are shown in Fig. 7. The OSL measurements were carried out using the 340-600 nm bandpass filter besides the monochromator for detection of the luminescence. That is why the OSL emission spectra are limited by this spectral range. As it is seen from Fig.7., in the same experimental conditions the OSL signal from the ceramics is the most intensive, then comes the nanorods, and the OSL signal from the nanotips is very weak. For all samples the OSL emission spectrum contains two bands: 400 and 470-480 nm. In the case of the ceramics the 400 nm band is predominant under irradiation at 240 nm, and the 480 nm band is the most intensive under irradiation in the 290 nm band. Excitation in the host lattice absorption region gives the relatively weak OSL signal. In the case of the nanostructures the highest intensity of the OSL signal is obtained under excitation in the spectral region of the host lattice absorption, and the shape of the OSL spectrum practically does not depend on the excitation wavelength.

![OSL emission spectra](image)

**Fig.7.** OSL emission spectra of AlN ceramics, nanorods and nanotips under excitation in the host lattice absorption region (thick solid line), at 240 nm (solid line) and the most long wavelength part of the absorption region (dotted line): 315 nm for ceramics and 276 nm for nanostructures.

The OSL excitation of ceramics for the 400 and 480 nm emission bands is shown in Fig.2. by curves 3 and 4. Similarly to the TL excitation spectra, these curves are mutually shifted, according to the corresponding PL excitation bands. The OSL excitation spectra of nanostructures for the 380 nm emission are seen in Fig.5. The OSL excitation spectrum of nanorods (curve 3) reveals a dominating feature in the 200-220 nm region, while the OSL excitation spectrum of the AlN nanotips (curve 4) is more evenly distributed in 200-300 nm range. The excitation spectra of the 480 nm bands of the nanostructures are not shown in the graph, because they are very much alike those of 400 nm bands.

4. **Discussion**

Comparing the spectral characteristics of the newly studied AlN nanostructures - nanorods and nanotips - with those of the already well known AlN ceramics it may be concluded that in general they are similar, particularly the emission spectra. The luminescence properties revealed under
irradiation with the UV light in the nanostructures can be assigned to the recombination processes with participation of the oxygen-related centers.

However, there are differences in the excitation spectra of PL, TL and OSL of the AlN ceramics and nanostructures. In the ceramics there is a strict correlation between the 400 nm emission band and 240 nm defect excitation band and 480 nm emission band and 290 nm defect excitation band, revealed in the spectra of PL, TL and OSL. From the TL measurements it follows that the short wavelength emission and excitation bands correspond to the low temperature TL peak, and the long wavelength bands – to the high temperature peak. Excitation in the host lattice absorption region produces both bands in the PL, TL and OSL emission spectra but the energy transfer is less efficient compared to the excitation in the defect absorption bands. It means that the luminescence process occurs mainly within 2 different pairs of close donor-acceptor centers. One of such pairs responsible for the 400 nm emission band was determined as an oxygen substituting for a nitrogen on a regular lattice site and an oxygen near aluminum vacancy [14]. Another pair of centers, giving the 480 nm luminescence, is not known for certain yet, but we can assume that these are oxygen-related centers in some perturbed environment (perhaps surface or interface) or agglomerated oxygen centers [3]. Moreover, from the TL results it may be concluded that each of such pairs is connected with its own trap center (or a set of trap centers), located in a close neighborhood and responsible for a definite TL peak.

In the nanostructures the excitation spectra of PL, TL and OSL (particularly those for nanorods) have the dominating part near the band edge, implying that the excitation process occurs mainly though the excitation of the host lattice and the further energy transfer. No distinct features of paired centers can be found from the luminescence measurements. The invariable shape of the OSL emission spectrum and TL curves means that the set of the trap centers participating in the light sum storage is the same irrespective of the excitation and emission wavelength. This speaks in favor of the random distribution of the centers participating in the luminescence and trapping processes in the nanostructure samples. This can be due to a smaller concentration of the defect centers, particularly oxygen-related, and the more perfect host lattice compared to that of the ceramics, defined by the sample production method and the raw material used.

Comparing the spectral properties of the nanorods and nanotips there are some differences seen. Thus, the near band edge region (195-210 nm) is more pronounced in the excitation spectra of PL, TL and OSL for nanorods, than for the nanotips. Besides, there is difference in the position of the TL peak: 80 ºC for nanorods and 100 ºC for nanotips. These peculiarities could be explained either by the modifications of the host structure and variations of the surface effect on defects energy levels during the growth of the samples or by the different concentration of the uncontrolled dopants, in particular oxygen.

5. Conclusions
The luminescence properties of the AlN nanostructures revealed under the UV irradiation are similar to those of the AlN ceramics, presumably they are induced by the recombination processes in the oxygen-related centers. The peculiarity of the nanostructures is that all the observed luminescence processes (PL, TL, OSL) are excited mainly through the host lattice absorption. That may be explained by the smaller concentration of the defect (oxygen-related and others) centres and the more perfect structure of the host lattice of the nanostructures compared to the ceramics. The small mutual differences revealed in the emission and excitation spectra and the TL curves of the AlN nanotips and nanorods possibly arise due to the modifications of the host lattice structure and variations of the defect concentration during the production of the samples.

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