

Cathodoluminescence of Oxygen-Vacancy Centers in Structures of Aluminum Nitride

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Abstract—Spectra of the cathodoluminescence (CL) of single crystals and micropowders of AlN are studied. It is shown that bands with maxima at 3.2, 2.7 and 2.1 eV can be observed in the CL. The peaks at 2.7 and 3.2 eV are associated with O_N centers and complexes of the type ($V_{Al}-O_N$); the 2.1 eV band is due to recombination processes involving cation vacancies. The narrow CL peak at 1.77 eV is also observed for AlN powder and is attributed to Cr^{3+} impurities.

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INTRODUCTION

Bulk single crystals of aluminum nitride were first obtained relatively recently [1]. In this structural modification, intense optical absorption for photons of the visible and ultraviolet ranges with energy below the band gap of 6.2 eV was observed. Strong luminescence in the spectral range of 300–600 nm is visible upon the optical or thermal stimulation of previously irradiated (UV, β) material [2, 3]. The same luminescence is thus associated with different centers and the processes that occur in the material. According to [4, 5], such luminescence could be due intrinsic defects in its structure: nitrogen vacancies (V_N centers), aluminum vacancies (V_{Al} centers), interstitial N and Al, or oxygen impurities (O_N centers) and different complexes based on it. The results from [2, 6] showed that the luminescent defects in specially undoped AlN single crystals are most likely of the oxygen vacancy and aluminum type, ($V_{Al}-O_N$ centers). Using additional fluorescent techniques to study and identify the optically active centers in AlN that are responsible for the observed radiation-induced emissions is obviously of great interest from both the fundamental and applied standpoints. The aim of this work was thus to study the spectral parameters of cathodoluminescence (CL) in different structures of aluminum nitride.

EXPERIMENTAL

We investigated bulk single crystals (S1–S13) obtained via sublimation–recondensation from fine aluminum nitride industrial powders [1]. According to mass spectroscopy, the content of oxygen impurities did not exceed 10^{18} cm^{-3} [7]. The diameter of all samples was 15 mm. Their thickness varied from 0.25 to 0.50 mm, and surface quality was epi-ready.

Microfine powder of AlN (P1), obtained by the subfluoride method [8], was chosen as our second object of study. An analysis of its chemical composition conducted by the manufacturer showed that the concentrations of impurities (O, Fe, C, Mg, Si) in the sample ranged from 0.6 to 0.7%. Spectral studies of the irradiated powders were performed in [9].

Cathodoluminescence spectra were measured on a KLAVI cathodoluminescence analyzer. Samples were irradiated at room temperature by electron beams with durations of 2 ns and an average electron energy of $130 \pm 10 \text{ keV}$ at a current density of 60 A/cm^2 . Spectra were recorded in the range of 350–750 nm. Exposure time was 50 ms.

RESULTS AND DISCUSSION

Figure 1 presents typical experimental CL spectra for the studied samples of aluminum nitride. It can be seen that dependences in the form of broad structured bands with several peaks with maximum energies $E_{\text{max}} \approx 3.2, 2.7, 2.2\text{--}2.0$, and 1.77 eV are characteristic of AlN.

The experimental CL spectra can be roughly divided into three groups. Dominance of the emission band with $E_{\text{max}} \approx 3.2 \text{ eV}$ is characteristic of samples S1, S2, S11, and S12 (group I). For samples S3–S10 and S13 (group II), there is a greater contribution from the luminescence band with $E_{\text{max}} \approx 2.7 \text{ eV}$. Note that the spectra of samples S2, S5, S11, and S12 are less intense with $E_{\text{max}} \approx 2.1\text{--}2.2 \text{ eV}$, while luminescence is not registered for other samples of single crystals of AlN in this spectral region.

Sample P1, having strongly marked emission bands with $E_{\text{max}} \approx 2.1$ and 1.77 eV, belongs to group III, for which luminescence of weak intensity is registered in the spectral range of 2.2–3.3 eV. Unlike samples S1–S13,

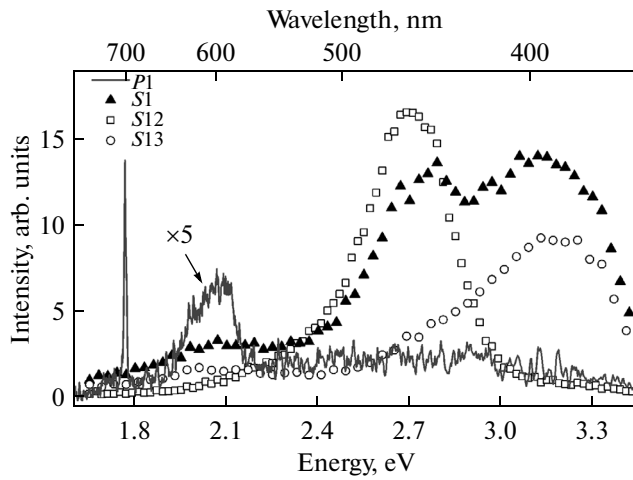


Fig. 1. Experimental CL spectra of the studied samples of AlN.

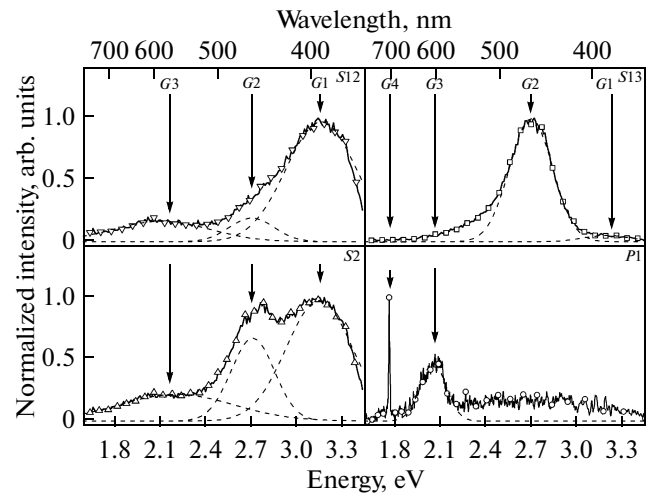


Fig. 2. Examples of the decomposition of CL spectra. Symbols denote experimental data; dashed lines, components in Gaussian form.

the luminescence band with $E_{\max} \approx 2.1$ eV thus dominates for sample *P1*, compared to the bands with $E_{\max} \approx 3.2$ and 2.7 eV.

For our analysis of the obtained data, all experimental CL spectra are described by superpositions of several Gaussian components. Examples of decomposition are shown in Fig. 2. The values of maximum energy E_{\max} resulting from approximation and the half-widths of peaks ω are shown in Table 1. The scatter of the calculated values of E_{\max} and ω was ± 0.04 eV. Analysis of the obtained values showed that four components can be distinguished in the CL spectra: *G1* ($E_{\max} = 3.2$ eV, $\omega = 0.45$ eV); *G2* ($E_{\max} = 2.7$ eV,

$\omega = 0.35$ eV); *G3* ($E_{\max} = 2.1$ eV, $\omega = 0.75$ eV); and *G4* ($E_{\max} = 1.77$ eV, $\omega = 0.05$ eV).

In analyzing the forms of the CL spectra of single crystals, it was found that the ratio between the maximum intensities of the dominant peaks I_{G2}/I_{G1} varied from sample to sample in the range of 0.2 to 22. The value of $I_{G2}/I_{G1} < 1$ is typical for samples of group I, while $I_{G2}/I_{G1} > 1$ was typical of group II. In addition, the values of E_{\max} and ω for the corresponding components remained constant within the errors, suggesting that the registered luminescence was due to the same types of defects, the concentrations of which are likely to depend on differences in the conditions of synthe-

Parameters of the Gaussian components of CL spectra decomposition

Group	Sample	<i>G1</i>		<i>G2</i>		<i>G3</i>		I_{G2}/I_{G1}
		E_{\max} , eV	ω , eV	E_{\max} , eV	ω , eV	E_{\max} , eV	ω , eV	
I	S1	3.17	0.43	2.74	0.39	—	—	0.86
	S2	3.16	0.51	2.72	0.34	2.22	0.89	0.69
	S11	3.17	0.45	2.73	0.37	2.15	0.76	0.75
	S12	3.17	0.54	2.71	0.34	2.12	0.75	0.19
II	S3	3.20	0.41	2.70	0.34	—	—	6.61
	S4	3.21	0.36	2.70	0.34	—	—	12.98
	S5	3.20	0.43	2.71	0.37	2.12	0.51	1.51
	S6	3.19	0.40	2.70	0.35	—	—	4.83
	S7	3.15	0.44	2.71	0.36	—	—	2.70
	S8	3.17	0.48	2.70	0.36	—	—	3.06
	S9	3.21	0.58	2.70	0.34	—	—	10.94
	S10	3.21	0.36	2.70	0.33	—	—	21.81
	S13	3.21	0.35	2.70	0.34	—	—	19.30
	III	P1—	—	—	—	—	2.06	0.20

sizing single crystals. In studying polycrystalline films of AlN [10], it was found that the intensity of bands *G1* and *G2* observed in photoluminescence (PL) spectra and their ratios were influenced by both internal lattice defects (V_N) and impurity oxygen and the complexes based on it. When the concentration of oxygen in the samples was decreased, the luminescence of *G1* grew. After heat treatment of the samples in a nitrogen atmosphere, *G2* intensity fell as the annealing temperature rose from 500 to 700°C.

Analysis of the published data revealed a luminescence band at 3.2 eV (*G1*) in the PL, CL, thermal (TL) and optically-stimulated luminescence spectra, and for different structures based on AlN (e.g., films, nanostructures, polycrystals, ceramics) [10–14]. This luminescence is a result of charge carriers transitioning from the shallow levels formed by anion O_N centers to the excited states of the levels of ($V_{Al}-O_N$) complexes with subsequent intracenter luminescence.

A luminescence band at 2.7 eV (*G2*) was also observed for powders [4], polycrystals [14], and nanotubes [15] in studies of PL, TL and CL processes, respectively. This luminescence is in some works [4] associated with deep levels formed by vacancy V_N centers. According to the results from other studies [14], the *G2* component is caused by O_N centers and the defects associated with them.

According to [16, 17], the weak luminescence at 2.1 eV (*G3*) in thin films and nanostructures could be due to such technological impurities as Mn contained in the initial material used in synthesizing samples. On the other hand, this band could be associated with the processes of recombination luminescence between the acceptor levels of cation V_{Al} centers and the valence band [5]. Since our analysis of the samples revealed no impurities of Mn, we may assume that the *G3* component was due to intrinsic defects (V_{Al}) of the crystalline lattice of AlN.

Intense narrow peak *G4* registered only for sample *P1* was probably due to the presence of uncontrolled Cr impurities in the initial precursors used in the sub-fluoride synthesis of AlN micropowder. This assumption is made on the basis of the independent analysis of the results for GaN in [18] and for Al₂O₃ in [19]. In those works, an intense narrow CL peak was also observed in the energy region of 1.75–1.79 eV; it was attributed to intracenter transitions ${}^2E \rightarrow {}^4A_2$ (*R* lines) of Cr³⁺ defects.

The results on CL obtained in this work were compared to the results from our earlier studies [2, 3, 6]. Figure 3 shows afterglow (AG), cathodo-, thermo-, and photoluminescence spectra, normalized with respect to the maximum.

It can be seen that the data obtained for different kinds of stimulation are in good agreement with one another. Note that the 2.1 eV component is clearly visible in the CL and TL spectra. The emission at 3.4 eV was observed in studies of the processes of afterglow,

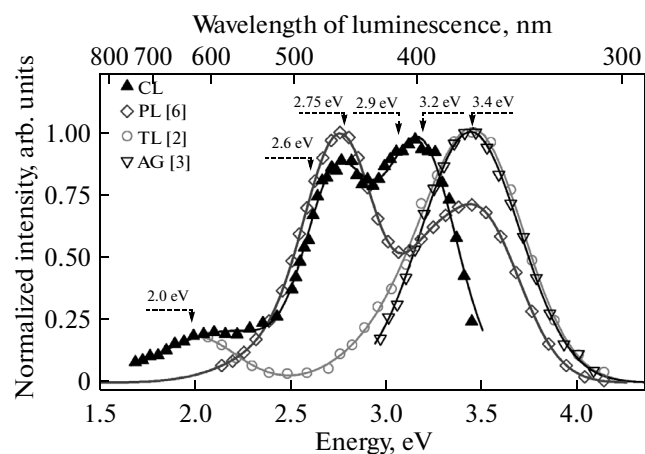


Fig. 3. Comparison of luminescence spectra (solid lines show the approximating curves of the experimental data).

thermo- and photoluminescence. Bands at 2.7 and 3.2 eV were registered in the CL and PL spectra. The 2.6 eV component, which can be detected when the corresponding luminescence curve is decomposed into Gaussians, is barely visible following photostimulation. Note that the band at 2.9 eV in the TL spectra is determined in the same way. We may therefore conclude that the same (intrinsic and extrinsic) types of point defects and defect complexes actively luminesce when irradiated single crystals of AlN are subjected to different types of stimulation.

CONCLUSIONS

Spectra of the cathodoluminescence of bulk single crystals and microfine powders of AlN were obtained and analyzed. It was found that the studied samples were characterized by dependences in the form of broad structured bands with several peaks. Bands at 2.1, 2.7, and 3.2 eV were present in the CL emissions of single crystals. It was found that the ratio between the maximum intensities of the dominant peaks at 2.7 and 3.2 eV varied from sample to sample in the range of 0.2 to 22. The CL spectra of AlN powder contained intense narrow peaks at 1.77 eV and wide band at 2.1 eV.

A comparative analysis was performed using our data and the results from independent studies. It was found that the same luminescence bands were recorded when using different ways of stimulating luminescence in the structures of AlN. It was shown on the basis of the literature data that main luminescent defects in such specially undoped crystals are oxygen impurities and complexes with cation and anion vacancies formed on the basis of them. The luminescence at 2.7 and 3.2 eV was a result of the recombination of donor–acceptor pairs, the levels of which are formed by such defects as oxygen–aluminum vacancy ($V_{Al}-O_N$). Recombination processes

between the acceptor levels of V_{Al} cation centers and the valence band result in the luminescence at 2.1 eV. The narrow band at 1.77 eV for AlN micropowder could be due to the presence of uncontrolled technological Cr^{3+} impurities.

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