Functional Materials 21, No.1 (2014)

Photoluminescence characterization of AlN nanowhiskers

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Received October 6, 2013

Photoluminescence (PL) properties of synthesized Al-rich nanowhiskers with diameter 60±20 nm and bulk AlN single crystals were compared at the room temperature. It was found that PL spectra for AlN nanowhiskers were characterized by three components of the Gaussian shape with maximum energy 3.16, 2.90, and 2.55 eV and halfwidth 0.7, 0.4, and 0.7 eV, respectively. It was shown that the same bands — 3.2 and 2.6 eV — were observed in luminescence of the bulk and nanostructured samples. The registered emissions were attributed to electron-optical transitions between donor levels of the O_N^-, V_N-centers and acceptor states of the C_N-centers and (O_N–V_{Al})-complexes.

Проведено сравнительное исследование фотолюминесцентных (ФЛ) свойств синтезированных в условиях избытка алюминия нановискеров с диаметром 60±20 нм и объемных монокристаллов AlN при комнатной температуре. Обнаружено, что спектры ФЛ для нановискеров AlN характеризуются тремя компонентами Гауссовой формы с энергиями максимума 3.16, 2.90 и 2.55 эВ и полушириной 0.7, 0.4 и 0.7 эВ соответственно. Показано, что в люминесценции исследуемых объемных и наноструктурных образцов присутствуют одни и те же полосы свечения — 3.2 и 2.6 эВ. Регистрируемые полосы отнесены к электрон-оптическим переходам между донорными уровнями O_N^-, V_N-центров и акцепторными состояниями C_N-центров и (O_N–V_{Al})-комплексов.

Дослідження фотолюмінісцентних властивостей AlN нановіскеров.
О.С Вохмінцев, І.О. Вайнштейн, Д.В. Чайкін, Д.М. Спірідонов, Ю.Д. Афонін

Проведено порівняльне дослідження фотолюмінесцентних (ФК) властивостей синтезованих в умовах надлишку алюмінію нановіскеров з діаметром 60±20 нм і об'ємних монокристалів AlN при кімнатній температурі. Виявлено, що спектри ФЛ для нановіскеров AlN характеризуються трьома компонентами Гауссової форми з енергіями максимуму 3.16, 2.90 і 2.55 еВ і напівшириною 0,7, 0,4 і 0,7 еВ відповідно. Показано, що в люмінесценції досліджуваних об'ємних і наноструктурних зразків присутні одні й ті ж смуги світіння — 3,2 і 2,6 еВ. Реєстровані смуги віднесено до електрон-оптичних переходів між донорними рівнями O_N^-, V_N-центрів і акцепторними станами C_N-центрів і (O_N–V_{Al})-комплексів.

1. Introduction

Filiform crystalline nanostructures or nanowhiskers of aluminum nitride are characterized by unique physical-chemical properties and offer a promising material for production of optical nanofiber, nanodetectors, and chemical-biological sensors [1, 2]. Due to weak electron affinity of <0.6 eV AlN nanowhiskers can be used for field emission cathodes [3]. At present different synthesis methods of AlN whiskers are known [1,4,5], but repetitive production requires a relatively simple growth technology for the filiform nanostructures with an spectr ratio more

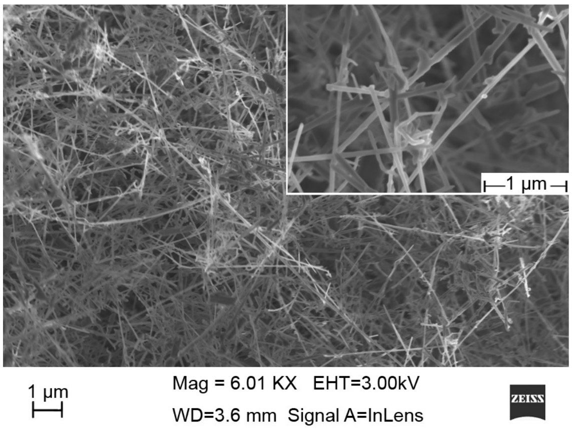

Fig. 1. SEM image of AlN nanowiskers.

than 100. Simultaneous treatment of liquid aluminum with gaseous aluminum chloride and nitrogen by condensation on the AlN polycrystalline substrate is one of such chemical technologies [7]. Isolated point defects and different complexes formed during this procedure essentially influence on the electrical and luminescent properties of the nanosized structures. Hence, the purpose of this study is to investigate the room temperature photoluminescent (PL) properties of AlN nanowhiskers.

2. Experimental

Two types of samples were studied: the AlN nanowhiskers, synthesis of which is described in detail in [6] and the bulk single crystals of AlN ("Nitride Crystals" Ltd.) in the form of substrates of 15 mm in diameter and 0.4 mm in thickness with the "epi-ready" surface. Growth conditions and chemical composition of the single crystals under study are given in [7].

Morphological characteristics of the nanowhiskers were studied with scanning electron microscope (SEM) Sigma VP Carl Zeiss. Chemical composition of the AlN whiskers was analyzed by an energy dispersion detector (EDS) X-max Oxford Instruments.

PL measurements of the nanowhiskers and bulk samples were carried out in phosphorescence mode at the room temperature using spectrometer LS55 Perkin Elmer. The PL spectra were registered within the range of λ_{em} = 290–900 nm, the excitation wavelength with the step of 5 nm varied in the region of λ_{ex} = 200–275 nm, with the scanning rate 60 nm/min.

3. Results and discussion

Fig. 1 shows the SEM images for the obtained AlN nanowhiskers with mean diameter 60±20 nm and the spectr ratio >100. According to quantitative chemical analysis, the element composition of the samples under study was as follows: Al – 42.7 at.%, N – 33.3 at.%, O – 18.5 at.%, and C – 5.5 at.%. From analysis of the data obtained, it can be seen that AlN nanowhiskers were synthesized with the lack of N and have the ratio Al:N ≈ 1:0.8. As distinct from the structures described in [1, 5], our samples are Al-rich type nanowhiskers with the high enough content of impure defects O_N and C_N, located at the positions of nitrogen atoms.

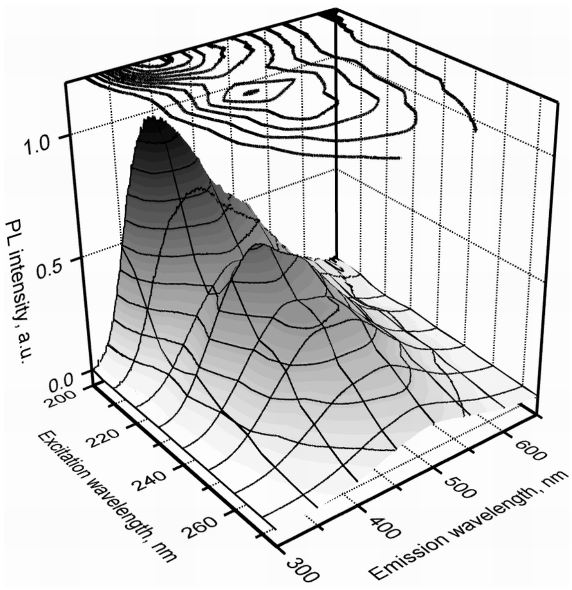

Fig. 2. 3D plot of PL spectra for AlN nanowhiskers.

Fig. 2 presents PL spectrum of the AlN nanowhiskers at the room temperature in the coordinates "excitation wavelength — emission wavelength — PL intensity". It is seen that a wide emission band with the maximum at λ_{em} = 394 nm is registered for λ_{ex} = 200 nm. With increasing λ_{ex} up to 275 nm the luminescence intensity falls approximately by 8.2 times, the maximum being shifted to the long-wave region with λ_{em} = 498 nm. It should be noted that the PL of the AlN whiskers were not observed within 600–900 nm spectral range under UV excitation in our study.

Fig. 3 shows decomposition of the PL spectra measured at λ_{ex} = 210 nm (a, b) and 250 nm (c, d) into a few components of the Gaussian shape for the AlN nanowhiskers (a, c) and AlN substrate (b, d). Table contains values of the maximum energy (E_{max}) and halfwidth (ω) for the luminescence bands obtained. The approximation accuracy in

Table. PL spectral parameters for AlN nanowhiskers and the bulk single crystal

Sample	Peak	Parameter	Excitation wavelength	
			210 nm	250 nm
Nanowhiskers	G1	E_{max}, eV	3.16	3.16
		ω, eV	0.73	0.73
	G2	E_{max}, eV	2.91	2.90
		ω, eV	0.27	0.43
	G3	E_{max}, eV	2.55	2,56
		ω, eV	0.69	0,68
Bulk crystal	G1′	E_{max}, eV	3.48	3.46
		ω, eV	0.51	0.52
	G2′	E_{max}, eV	3.15	3.18
		ω, eV	0.40	0.28
	G3′	E_{max}, eV	2.70	2.77
		ω, eV	0.65	0.42
	G4′	E_{max}, eV	–	2.55
		ω, eV	–	0.61

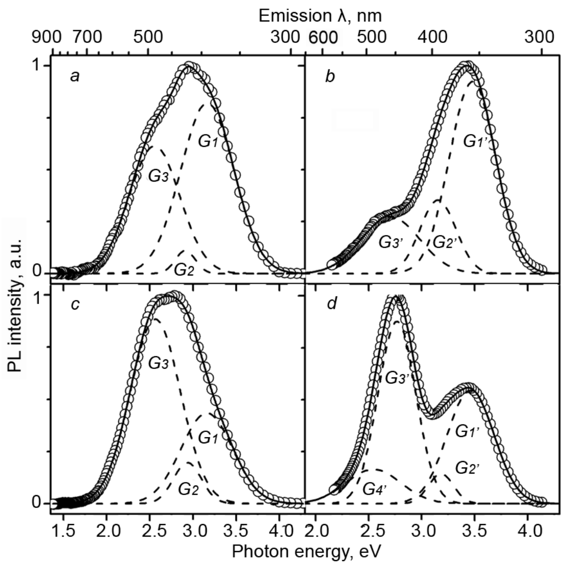

Fig. 3. Emission spectra approximation for AlN nanowhiskers (a, c) and the single crystal (b, d) by excitation in λ_{ex} = 210 nm (a, b) and 250 nm (c, d) bands. Symbol — experimental data, solid line — approximation, dot line — the Gaussian peaks.

this case is $R^2 > 0.999$, while the estimation error of the parameters is $\Delta E_{max} = \pm 0.01$ eV and $\Delta\omega = \pm 0.02$ eV for all the experimental spectra. Note that the investigated UV spectra of the AlN bulk- and nanosamples have identical emission components, i.e.: 3.1–3.2 eV (G1 and G2′ peaks in the nanowhisker and substrate, respectively) and 2.5–2.6 eV (G3 and G4′ peaks in the nanowhisker and substrate, respectively). Earlier the similar emission bands were registered in the PL spectra for AlN–Y_2O_3 ceramics, AlN nanostructures and polycrystalline AlN films [9, 10]. They were attributed to oxygen-related centers and nitrogen vacancies V_N. It should be noted that 3.4–3.5 eV band (G1′ peak for the substrate) was also observed in the spectra of the afterglow, cathodo-, thermo- and optically stimulated luminescence for the AlN single crystals and whiskers [2, 11–14] and it was supposedly caused by oxygen-related centers.

High oxygen content (18.5 at. %) in the synthesized Al-rich whiskers may point to formation of the O_N-centers and low concentration of aluminum vacancies V_{Al} in a crystal lattice. In this case there is an increased probability of forming the (V_{Al}–O_N)-complexes in different charge states. Moreover, adsorption of molecular O_2 may occur on the surface of the AlN nanowhiskers [4].

For illustration, Fig. 4 demonstrates the normalized data in comparison with the PL spectra for the AlN whisker structures from independent [1, 4]. It is seen that spectral

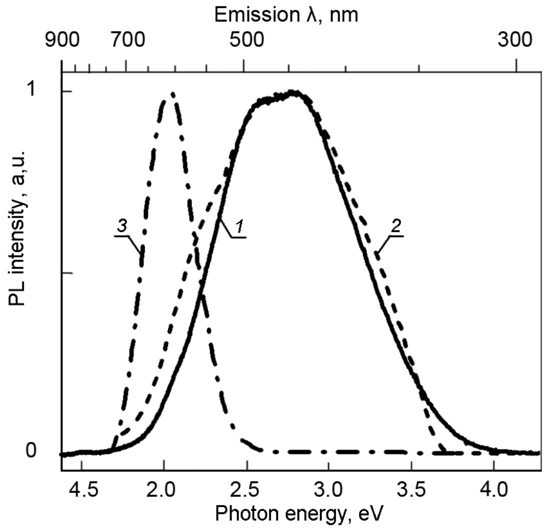

Fig. 4. Normalized PL emission spectra for AlN whiskers. Curve *1* – our experimental data (λ_{ex} = 250 nm); curve *2* – the spectrum from [4] (λ_{ex} = 300 nm); curve *3* – the spectrum from (λ_{ex} = 325 nm).

position and the shape of curves *1* and *2* agree well. Actually, in [4] (curve *2* in Fig. 4), the Al-rich whiskers were also grown using inert atmosphere and powder mixture (Al, Fe_2O_3) in ratio 3:1, resulting in a decrease of the growth temperature down to 900°. The PL spectra [4] were decomposed into three components of the Gaussian shape, for which the values of E_{max} = 3.0 eV (416 nm), 2.6 eV (480 nm), and 2.2 eV (564 nm) are close to ours.

Fig. 4 also demonstrates the PL spectrum for the AlN whiskers (curve *3*) characterized by an intensive emission band of 2.0 eV (612 nm) [1]. Note that earlier the 2.0 eV band was observed in thermoluminescence spectra of the AlN bulk single crystals under study [14]. The authors of [1] assigned this band to transitions between the levels of isolated V_{Al}-centers and the valence band. In fact, in [5] the N-rich AlN whiskers are synthesized under the conditions of aluminum lack, with the ratio Al:N = 0.8:1, resulting in predominance of the isolated V_{Al}-centers and low concentration of the (V_{Al}–O_N)-complexes and O_N-centers due to low oxygen concentration. Hence, absence of the 2.0 eV band in our spectra supports the hypothesis about the presence of aluminum vacancies in the (V_{Al}–O_N)-complexes in Al-rich whiskers. Due to the same reason 3.2 eV emision caused by donor-acceptor recombination between the O_N-center and (V_{Al}–O_N)-complex is negligible for N-rich whiskers [1] and dominates in the PL spectra for Al-rich whiskers at excitation 5.9 eV (210 nm) in the present study.

From analysis of independent data, emission in 2.55 eV band (component G3 in Figs. 3a,c) can be also attributed to the optical transitions with participation of the (V_{Al}–O_N)-complexes. These transitions may occur between the levels of the V_N-center in vicinity of the conduction band bottom and the ground level of the (V_{Al}–O_N)-complex in vicinity of the valence band top [4]. At the same time, from the PL investigation of the AlN samples with developed surface (nanopowder, nanorods, nanotips), emission in 2.6 eV band was attributed to internal transitions of the (V_{Al}–O_N)-complex [9].

Earlier 2.91 eV emission (G2 in Fig. 3a,c) was registered in photo-, cathodo-, thermo-, and optically stimulated luminescence for single crystals, powders and nanostructures of AlN [13–17]. As a rule, this emission was attributed to the donor-acceptor recombination of the O_N-centers and (V_{Al}–O_N)-complexes [17] or to the processes involving carbon impurities [13, 16]. For example, in the AlN single crystals 2.8 eV emission was observed under 4.7 eV excitation with the high concentration of carbon and the maximum was shifted towards the red region with decreasing excitation energy [16]. The luminescence was ascribed to recombination between the donor nitrogen vacancies and acceptor levels of the C_N-center (carbon atom in the position of nitrogen). With account for high content of carbon (5.5 at.%) in the Al-rich nanowhiskers under study the observed 2.91 eV emission may be due to radiative processes involving V_N- and C_N-defects in the anion sublattice.

4. Conclusions

The Al-rich AlN nanowhiskers with average diameter 60±20 nm and the ratio Al:N = 1:0.8 were synthesized. According to chemical analysis the obtained samples are characterized by the high content of oxygen (18.5 at.%) and carbon (5.5 at.%) impurities. This fact allows assuming preferable formation of isolated O_N^-, C_N^-, and V_N-centers and oxygen-vacancy (V_{Al}–O_N)-complexes of different charge in the crystal lattice of the filiform structure under study.

The PL properties of the synthesized nanowhiskers and bulk AlN single crystals were compared within the 4.28–1.38 eV (290–900 nm) spectral range under excitation in the region of 6.20–4.51 eV (200–275 nm) at the room temperature. All of the PL spectra for the AlN nanowiskers were found to have three components of the Gaussian shape with the maximum energy $E_{max} \approx 3.16$, 2.90, and 2.55 eV and halfwidth $\omega \approx 0.7$, 0.4, and 0.7, respectively. It is shown that the analyzed luminescence of the bulk and nanostructured samples is characterized by the presence of the same emission bands: 3.1–3.2 eV and 2.5–2.6 eV. Analysis of the obtained experimental data and comparison with the results of independent studies of aluminum nitride in different structural forms allows to attribute the registered bands to the electron-optical transitions between donor levels of the O_N^-, V_N-centers and acceptor states of the C_N-centers and (O_N–V_{Al})-complexes.

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