F-center Luminescence and Oxygen Gas Sensing Properties of AlN Nanoparticles

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Abstract: Luminescence caused by native defects in AlN nanoparticles (NP) with average diameter of 60 nm were studied using spectral characterization of the material. Photoluminescence and its excitation spectra were measured within a wide temperature interval between 300 – 8 K, and spectral range including ultraviolet (UV) and visible light. Luminescence properties were studied when a sample was surrounded by different media (vacuum and several gases such as oxygen, nitrogen, argon, air, oxygen-nitrogen mixtures). A blue luminescence (BL) consisting of two main sub-bands at 390 nm and 410 nm for AlN NP was observed. Two spectral regions around 315/340 nm and 260 nm were distinguished, including defect-induced absorption resulting in excitation of the BL. It was found that there are two different defect-induced luminescence mechanisms causing the BL. One of them is an intra-center mechanism and the other one is recombination luminescence mechanism, and their efficiency is highly dependent on spectral region of exciting light. It was found that oxygen gas which is surrounding the sample is reducing intensity of the BL. The oxygen gas sensing properties of AlN NP were studied allowing assumption that material is prospective for the development of oxygen gas optical sensors. As a result of this research the native defects responsible for the BL were related to nitrogen vacancy type defects known as the so-called F-centers. These defects can be located both on the surface and in bulk of the material, and the surface defects whose role is predominant in nanoparticles are responsible for oxygen sensing properties of AlN NP.

Keywords: Aluminum nitride, nanoparticles, luminescence, F-centers, oxygen gas sensing.

1. Introduction

At present elaboration and investigation of various luminescent nanomaterials is with great importance due to their small size and new excellent properties, which are decisive for the development of smart technologies and other applications. Large number of prospective material applications is based on their optical properties. Among these materials the wide band gap semiconductors are of special interest due to their absorption/luminescence spectra are covering a wide spectral range including visible and far ultraviolet (UV) light.

AlN is one of prospective wide band gap ($E_g$>6 eV [1-3]) materials with wurtzit crystalline structure [4] being accessible in forms of the bulk materials such as single crystals and ceramics, as well as in different types of nanostructures including nanopowders, nanorods, nanotips and others. Optical properties of the material are highly dependent on intrinsic defect types and the so-called point defects are the most important among them [5, 6]. There is a large number
of various defect types characteristic for the wide band gap materials including the so-called native defects which are inherent to the material without its special treating. The defects caused by the elements of the host material are the most typical among them. For AlN the most common are nitrogen and aluminum vacancies (v\textsubscript{N} and v\textsubscript{Al}, correspondingly), interstitials (i\textsubscript{N} and i\textsubscript{Al}) together with some native dopants such as oxygen and carbon atoms substituting for nitrogen (O\textsubscript{N}, C\textsubscript{N}) [7 and Refs. therein] and others. All these defects also can form different complexes.

The aim of the present study is determination of luminescent native defects inherent for AlN nanopowder together with revealing of luminescence processes and mechanisms caused by these defects as well as indication to some possible applications of this material based on its luminescence properties.

2. Material and Experimental

AlN nanopowder (NP) consisting of polycrystalline grains with average size of 60 nm was synthesized in Institute of Inorganic Chemistry, Riga Technical University by using plasma-chemical synthesis [8]. Raw aluminum powder (99.4 %) with particle size in the range of 20-40 μm was injected and evaporated into nitrogen (99.9 %) high-frequency plasma flow. In order to promote formation of AlN and to reduce particle growth ammonia was introduced additionally in high temperature flow containing aluminum vapors.

Photoluminescence (PL) and excitation (PLE) spectra of AlN NP were measured using a home-made setup, consisting of the following parts: i) a sample holder mounted inside of the sample chamber of a closed cycle refrigerator (CCS-100/204, Janis Research Corporation), allowing to perform spectral measurements at different fixed temperatures inside the interval 8 – 300 K, when sample is in vacuum, besides, the sample chamber can be filled with various gases allowing measurements at room temperature; ii) a light source – a deuterium lamp (LD-400) for luminescence excitation and iii) a luminescence recording system containing the grating monochromator (Andor Schamrock SR-303i-B) together with the photomultiplier (Hamamatsu H7468-03) or CCD camera. All necessary spectral corrections related to the measurements are taken into account.

For spectral measurements AlN NP pressed in small tablets with 13 mm diameter and 1-2 mm thickness were used.

3. Results and Discussion

3.1. Native Defect Caused Luminescence of AlN Nanoparticles

Photoluminescence and its excitation spectra of AlN NP were measured for samples surrounded by vacuum (~10\textsuperscript{-5} mbar) at different fixed temperatures between room temperature (RT) and 8 K. Luminescence kinetics of PL also was studied at RT. Besides, the PL characteristics were examined when samples were surrounded with different gases including oxygen, nitrogen, argon, air and oxygen/nitrogen mixtures.

3.1.1. Photoluminescence Characteristics

Photoluminescence and its excitation spectra of AlN NP measured at RT when sample is in vacuum are depicted on Fig. 1, a and b, correspondingly.

![Fig. 1. AlN NP, RT. (a) PL spectrum at 315 nm or 260 nm excitation divided in three Gaussian curves (dash lines), (b) PLE spectrum of BL, where two spectral intervals are marked (I and II).](image-url)
spectrum there are two main and highly overlapping bands at 340 nm and 315 nm, whereas, at the shorter wavelengths around 260 nm another wide and complex excitation band appears. Accordingly to this structure of the PLE spectrum, two different spectral intervals are marked as I and II on Fig. 1. b. Irradiation of material with light from the spectral region around 200 nm also results in appearance of the BL, which can be related to the exciton processes causing this luminescence. Excitation intervals I and II, with lower energies than that of exciton, are related to absorption of native defects. It is found that at RT the shapes of the BL spectra excited with light from the spectral intervals I and II are coincident.

PL spectra of ALN NP were measured at different fixed temperatures inside the range of 300 K – 8 K.

A set of the PL spectra, measured at different fixed temperatures under excitation of ALN NP with 315 nm light from the first spectral interval (Fig. 1, b) is shown in Fig. 2. a. It is seen that at various temperatures the shape of the luminescence band does not change essentially, whereas luminescence intensity is growing with decrease of temperature. These PL spectra measured at different temperatures of sample were used for building up Arrhenius plot of the integral luminescence intensity (ILI) on reverse temperature, which is seen on Fig. 2, b. For determination of the ILI the central part of the PL spectra framed by dotted straight lines depicted on Fig. 2, a, which includes the PL sub-bands at 290 nm and 410 nm, was used. As it is seen from the Fig. 2, b, there are two temperature intervals between 300 K – 100 K and 40 K to 8 K, where the graph is presented by a straight line. Inside of the high temperature interval 300 K - 100 K decrease of temperature results in increase of ILI and an observed linearity of the graph is characteristic for the simple exponential processes. Inside the low temperature interval from 40 K to 8 K the process is characterized by practically horizontal straight line, which demonstrates independence of the BL intensity on temperature. In general, such type processes described above are characteristic for the intra-center luminescence [9].

Dependence of the PL spectra of ALN NP on temperature under 260 nm excitation related to the II spectral interval of excitation (Fig. 1, b) was also investigated. In this case, besides the BL, which is observable at RT, another wide and complex luminescence band around 500 nm appears at temperatures below 200 K. Decrease of the sample temperature results in intensive increase of 500 nm luminescence intensity, which is highly exceeding that of the BL intensity thus modifying its spectral shape. The excitation spectrum of the 500 nm luminescence differs from that of the BL thus allowing assumption that both the BL and the luminescence at 500 nm are caused by various defect types.

Kinetics of the BL under excitation at 215 nm was studied at RT. It was found that after ceasing of exciting light the PL pulse is presenting an exponential decay, which can be characterized with short decay time in order of $10^{-7}$ s.

During investigation of the PL spectra of ALN NP it was observed that the highest intensity of the BL appears when the sample is in vacuum, whereas, ambient air surrounding the sample decreases the BL intensity. A special study of this phenomenon was performed.

The BL spectra of ALN NP were measured at RT, when the sample is surrounded not only by vacuum, but also by different gases (Fig. 3). It was found that the BL of ALN NP is sensitive to surrounding oxygen gas, which is quenching the luminescence intensity (Fig. 3, curves 2 and 3). In the same time, other gases such as nitrogen and argon have not influence on the BL intensity, being concurrent with that observed when sample is in vacuum (Fig. 3, curve 1).

Sensitivity of BL to oxygen gas was tested and observed also in commercial ALN powder with average grain size exceeding 100 nm.

The observed phenomenon allows conclusion that the BL is mainly caused by the surface defects. When theses surface defects interact with surrounding oxygen a new type defects are created, which are different from those causing luminescence. Nevertheless, the BL is not completely quenched even when the sample is surrounded by pure oxygen gas.
(Fig. 3, curve 3), thus allowing conclusion that in this case the observed BL is caused by the luminescent defects from in the bulk material of AlN grains. As it is seen from the Fig. 3, curves 1, 2 and 3, the shapes of all three PL spectra are coincident. It allows assumption, that the position of the luminescent defect being situated either on material surface or in its bulk does not affect significantly a structure of the luminescent defects.

In summary, the results observed allow conclusion, that the defects which are causing the BL in AlN NP can be located in both the bulk of material and on its surface. In the case of nanomaterial the amount of surface defects exceed that from the bulk material due to extremely large specific area characteristic for the nano-grains.

3.1.2. Oxygen Sensing Properties of AlN NP

Oxygen sensing properties of AlN NP were examined. One of the most important characteristics describing oxygen gas sensing properties of AlN NP is repeatability of the response. This property is examined in the following way: the medium surrounding of the AlN NP sample was changed from vacuum to pure oxygen gas and backwards and this procedure was repeated ten times. In each of these states the luminescence spectrum was measured and its ILI was evaluated. The results are seen on the left side Fig. 4, where the ILI is depicted by the full circles (1) when sample is put in vacuum ~10^{-5} mbar or by the hollow circles (3) when the sample is surrounded by oxygen gas. The full squares (2) represent relation of the mentioned values. As it is seen from the Fig. 4 the repeatability of the results is good and AlN NP possesses qualities which are significant for oxygen gas sensors.

Dependence of the BL intensity on oxygen concentration in gas mixture surrounding the AlN NP material was studied. The commercial oxygen-nitrogen gas mixtures with different oxygen concentrations were used and the results are seen on Fig. 4, the right side. A nonlinear increase of the luminescent response, measured as ratio of ILI when sample is in vacuum and gas mixture, with increase of oxygen concentration is observed. The first point on this curve represents a case when the sample is in vacuum, but the last one – when the sample is surrounded with a pure oxygen gas. As it is seen from the picture the curve demonstrates a fast increase within a region of low oxygen concentrations below 10 %. Therefore, a more prospective use of the AlN NP as material for oxygen gas sensors could be related to the low oxygen concentrations (below 10 %) in gas mixtures. Nevertheless, the region of oxygen concentrations around 21 %, which is characteristic for ambient air, also seems to be considerable.

In summary, the observed spectral properties of AlN NP allow its ranking as the material useful for development of oxygen gas optical sensors.

3.2. Luminescence Mechanisms

Analysis of the BL spectral characteristics of AlN NP discussed above allows revealing of several
luminescence mechanisms, responsible for the BL, and each of them is highly dependent on conditions of luminescence excitation. For illustration of the processes, which are representing different luminescence mechanisms a scheme of AlN energy band structure and energy level states of two different defects (A and D) is depicted on Fig. 5.

![Diagram of AlN Energy Band Structure](image)

**Fig. 5.** Schematic representation of an energy band diagram of AlN (CB - conduction band and VB - valence band); energy levels of two different defects A and D, consisting of the ground states (1 and 3) and excited states (2 and 4), correspondingly, as well as trapping states for electrons (5) and holes (6). Bold vertical and oblique arrows are representing optical transitions between various defect states, but horizontal arrows are depicting the defect excitation (\(Ex(I)\), and \(Ex(II)\)) and emission (BL).

It is possible suggest that for AlN NP there are two main native defect-induced mechanisms causing the BL. One of them is an intra-center mechanism, when the light absorption and emission occur inside one and the same defect. This mechanism is realized when the exciting UV light corresponds to the spectral interval I shown on Fig. 1, b. Existence of this mechanism is affirmed by the following facts. i) Position of the maxima of the luminescence bands and excitation bands from spectral interval I is very close and difference between them (the so-called Stock shift) does not exceed 1 eV (Fig. 1, a, and b). ii) Dependence of BL intensity on temperature within a region from 300 K to 8 K discussed above also affirms presence of intra-center processes. iii) The decay time of the BL in order of \(10^{-5}\) s is characteristic for the intra-center processes. This intra-center luminescence mechanism is depicted on Fig. 5, realizing for the defect A, when absorption of light quantum (\(Ex(I)\)) induces optical transition \(1\rightarrow2\) between the ground and excited energy states (1 and 2, respectively) and subsequent BL emission caused by transition \(2\rightarrow1\). All processes occur inside one and the same defect A.

When the exciting light is corresponding to the spectral interval II (see Fig. 1, b), then the BL most credibly is caused by recombination processes. In this case there are two different but mutually interacting defect types, depicted as A and D on Fig. 5. One of them (D) is responsible for light absorption from the spectral region II (\(Ex(II)\)), but the other one (A) - for light emission (BL). Besides, in this case the defect A is the same as that one originating the intra-center luminescence, because the shapes of corresponding luminescence spectra are coincident at RT. Presence of luminescence recombination mechanism is confirmed by the following considerations. i) From the Fig. 1, a, and b it is seen that the positions of the BL emission bands and excitation band from the spectral interval II are considerably separated demonstrating a large value of the Stock shift, that is not typical for the intra-center processes. ii) In the same time, it is known that irradiation of bulk AlN with light from the II spectral interval results in realization of different recombination processes, including recombination luminescence of the so-called oxygen-related defects [10-14] and energy storage in the material, which can be released through thermally or optically stimulated processes [15-17]. These observations together allow consideration that the recombination mechanism is causing the BL observed in AlN NP at irradiation with UV light around 260 nm from the spectral interval II depicted on Fig. 1, b.

Beside these two native defect-induced BL mechanisms an energy transfer mechanism from excitons to luminescent defect followed by BL emission is also present when the sample is excited with light from the far UV spectral region around 200 nm (see Fig. 1, b, a).

### 3.3. Luminescent Native Defects in AlN NP

Results of the present investigation together with an analysis of appropriate data from the scientific literature allow determination of defect types which are responsible for the BL in AlN NP.

At first we can exclude the well-known oxygen-related defects (ORD) observed in the bulk AlN, which also emit light from the blue spectral region, because the PL and PLE spectra of ORD [7, 10-14] essentially differ from those observed in the present study. Nevertheless, the spectral region of exciting light around 260 nm is common for both the ORD and the defects causing the BL in AlN NP. Therefore, we cannot completely exclude presence of ORD, when AlN NP is excited with light around 260 nm, but influence of ORD is physically impossible when sample is excited with light from the first spectral region seen on Fig. 1, b.

The most possible defect types which could be responsible for the BL in AlN NP are nitrogen vacancy type defects. Already in the early work of Y.C. Lan et al. [18] the PL at 477 nm in AlN powder was tentatively attributed to \(V_N\) centers. At present there is a lot of theoretical works stating that \(V_N\) forms a deep donor level in a wurtzite AlN structure [19-24]. Such position of defect state is necessary condition allowing assumption, that not only the \(V_N\) type defect ground state but also its excited state are placed inside the wide band gap of AlN. Then energy difference between these states could be big enough to cover
spectral interval where the PL and PLE spectra are observed in the present study (see energy scheme on Fig. 5).

As is known, the $v_N$ can capture electrons due to compensation of electrical charge in the crystalline lattice of the material thus forming the so-called F-centers [25]. For AlN there are three types of the F-centers named F, F$^+$ and F$^{2+}$ which are created when 3, 2 or 1 electrons are added to the $v_N$. Such variety of the F-center types can explain the complex structure of the PL spectra.

In summary, we assign the defect types which are originating the blue luminescence in AlN NP to nitrogen vacancy type defects or the so-called F-centers. These defects can be located both in a bulk of material or on its surface. In the case of nano particles the surface defects can be dominant. There is a valid argument speaking in favor of this assumption. The blue luminescence is observed also in hBN and its features are very close to those observed in AlN NP [26]. Unifying element for both hBN and AlN is the nitride sub-structure of host material, where the $v_N$ centers are formed.

4. Summary

Spectral characteristics of AlN nanopowder were studied. It was found that in AlN NP a defect-induced blue luminescence appears forming a wide complex band peaking at 415 nm, consisting of several sub-bands where the main of them are at 390 and 410 nm. This BL can be excited with light from two defect-related absorption regions situated around 315/340 nm and 260 nm. Depending on the excitation regions, two luminescence mechanisms causing the BL in AlN NP were found. One of them is the intra-center mechanism, which occurs when sample is irradiated with light from the long wave spectral region at 315/340 nm. The other one is the recombination luminescence mechanism, which can be activated with light from the short wave spectral region around 260 nm.

Analysis of our experimental results together with those reported in the scientific literature allow assumption that the native defects which are responsible for the BL luminescence in AlN NP can be related to nitrogen vacancy type defects known as the F-centers.

It was found that the BL in AlN NP is sensitive to surrounding oxygen gas which is quenching luminescence intensity. These investigations allow conclusion that the BL is caused by both the surface defects and those from the bulk material. In nano material role of the surface defects is predominant. Good gas sensing properties such as repeatability of the response and others were found. Sensibility of the BL of AlN NP to surrounding oxygen gas is ranking material among those being prospective for a development of oxygen gas optical sensors.

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References


