

# PHOTOLUMINESCENCE OF FS-GaN TREATED IN ALCOHOLIC SULFIDE SOLUTIONS

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## **Abstract**

Results are presented on the photoluminescence of n-GaN ( $T=300$  K) after surface treatment with sulfide ( $\text{Na}_2\text{S}$  and  $(\text{NH}_4)_2\text{S}$ ) solutions in water or isopropyl alcohol.

It has been shown that the intensity of the n-GaN photoluminescence band is enhanced as a result of the surface treatment with alcoholic sulfide solutions, this enhancement being greater for a strongly basic  $\text{Na}_2\text{S}$  solution than for a weakly basic  $(\text{NH}_4)_2\text{S}$  solution.

## **Introduction**

The progress in UV semiconductor optoelectronics relies not only on the advance of fabrication methods of III-V nitrides but on the surface treatment methods as well. In the last years a number of studies [1-3] was published dealing with modification of the electronic properties of the GaN surface treated with liquid or gaseous agents. For chemical treatment in solutions, both acids and bases are used: HCl, HF,  $\text{NH}_4\text{F}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NH}_4\text{OH}$ , NaOH, KOH [3]. Studies of the electronic properties of III-V semiconductor surfaces aim first of all at reducing the surface recombination velocity, increasing the photoluminescence quantum yield and so on. To achieve modification of the surface electronic properties, aqueous [4] or alcoholic [5] solutions of sulfides ( $\text{Na}_2\text{S}$  and  $(\text{NH}_4)_2\text{S}$ ) can be used.

In this study an attempt was undertaken to apply the technology of surface passivation employing alcoholic sulfide solutions in order to improve the electronic properties of GaN, in particular, the photoluminescence intensity.

## **Experiment**

The specimens under study were n-GaN layers ( $n=5 \times 10^{18} \text{ cm}^{-3}$ ) of a thickness 200-400  $\mu\text{m}$  grown on sapphire substrates by chloride gas transport epitaxy [6]. After termination of the epitaxial growth process the layers were separated from the substrate (free-standing GaN).

Chemical treatment of the GaN surface was performed by dipping the semiconductor specimen at room temperature for 1 min into one of the following solutions: 10% aqueous solution of  $(\text{NH}_4)_2\text{S}$ , 1% solution of  $(\text{NH}_4)_2\text{S}$  in isopropyl alcohol ( $i\text{-C}_3\text{H}_7\text{OH}$ ), and saturated  $\text{Na}_2\text{S}$  solutions in water or isopropyl alcohol.

The room temperature photoluminescence was excited with a pulsed nitrogen laser ( $\lambda=337 \text{ nm}$ ,  $I=20 \text{ W}$ ). The experimental setup was similar to that of Ref. [7].

## **Results**

The experimental results are as follows. The photoluminescence intensity of n-GaN increased as a result of the sulfide treatment of the surface in solutions of both sodium sulfide and ammonium sulfide (Fig.1). The most pronounced intensity increase (by a factor of 3.6) compared with the intensity of untreated n-GaN was observed for treatment with the saturated solution of  $\text{Na}_2\text{S}$  in isopropyl alcohol.

The increase in the GaN photoluminescence intensity following treatment with sulfide solutions in isopropyl alcohol can possibly be explained using mechanisms of the chemical processes taking place during sulfidizing of GaAs surface[8]. Sodium sulfide is known to be a salt of a strong base and a weak acid whereas ammonium sulfide is a salt of a weak base and a weak acid. It is therefore evident that in the case of treatment with alcoholic solutions of sodium sulfide the rate of chemical reaction with the GaN surface should be higher than for treatment in alcoholic solutions of ammonium sulfide. In the chemical treatment of III-V semiconductor surfaces (GaAs) the chemical reaction rate is the dominant factor affecting electronic properties of the surface [8], and it can be presumed that this should be true in the instance of III-V nitrides as well. Considering the fact that the chemical reaction rate for the aqueous sodium sulfide solutions is the lowest among the solutions used, it is no wonder that the effect of the chemical treatment of GaN surfaces in these solutions is practically unobservable (Table I).

As seen from a comparison of the photoluminescence intensity of GaN observed in this study and that of GaAs treated with strongly basic salts ( $\text{Na}_2\text{S}$ ) and weakly basic salts ( $(\text{NH}_4)_2\text{S}$ ) as measured in Ref.9, the photoluminescence intensity enhancement in both semiconductors is in good agreement with the adopted reaction mechanisms [8].

It should be note that similar increasing of photoluminescence intensity observed after the anneal of GaN at a temperature of 1000 °C or the sputtering with nitrogen ions [10].

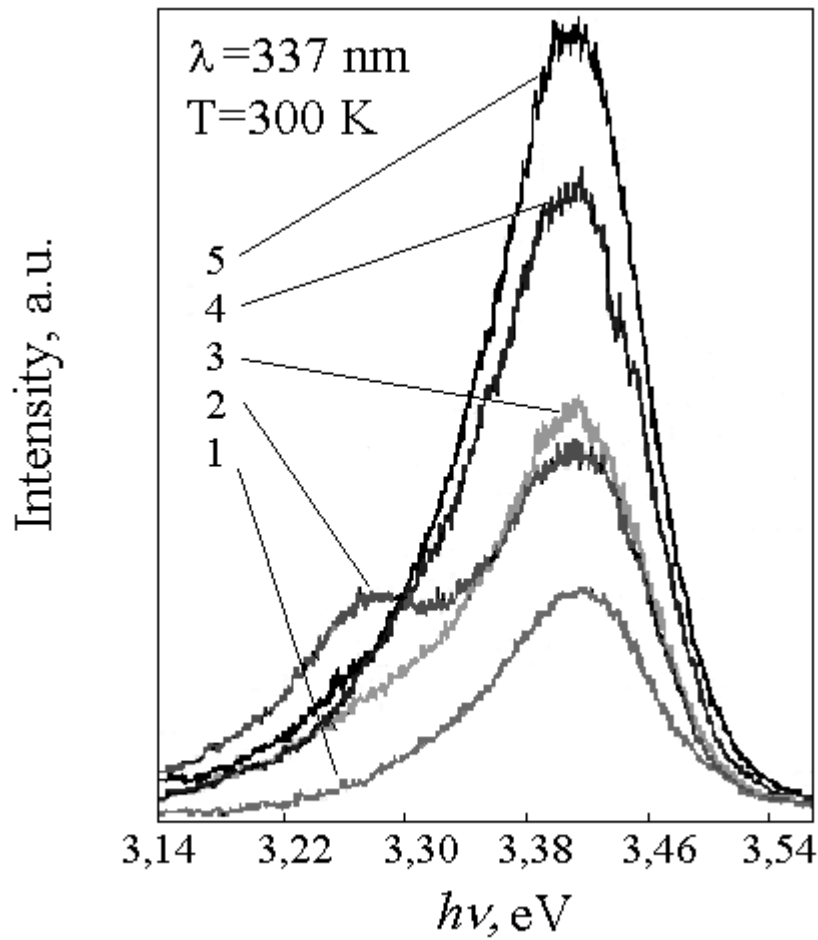


Fig.1. Photoluminescence spectra of the n-GaN surface after sulfidizing in one of the following four solutions: 10% aqueous solution of  $(\text{NH}_4)_2\text{S}$  (2), 1% solution of  $(\text{NH}_4)_2\text{S}$  in isopropyl alcohol ( $i\text{-C}_3\text{H}_7\text{OH}$ ) (3), and saturated  $\text{Na}_2\text{S}$  solutions in water (4) or isopropyl alcohol (5). The photoluminescence peak intensity of untreated GaN (1) is assumed to be unity.

Table I. The observed intensities of the photoluminescence peaks of GaN and GaAs [9] after various chemical treatments in sulfide solutions.

<i>Treatment</i>	<i>GaN</i> ( $n=5 \times 10^{18} \text{ cm}^{-3}$ )	<i>GaAs</i> ( $n=1 \times 10^{18} \text{ cm}^{-3}$ ) [9]
	I, a.u.	I, a.u.
untreated	1,0	1,0
$(\text{NH}_4)_2\text{S} + \text{H}_2\text{O}$	1,7	1,5
$(\text{NH}_4)_2\text{S} + i\text{-C}_3\text{H}_7\text{OH}$	1,9	1,7
$\text{Na}_2\text{S} + \text{H}_2\text{O}$	2,9	1,5
$\text{Na}_2\text{S} + i\text{-C}_3\text{H}_7\text{OH}$	3,6	2,3

## Conclusions

- Thus, a new technique of GaN surface passivation - sulfidization in alcoholic solutions has been suggested. The chemical treatment of the n-GaN surface with sulfide solutions in isopropyl alcohol appears to reduce the surface states density. The degree of the photoluminescence intensity increases reached with solutions of the sulfide of a strong base [Na<sub>2</sub>S] is larger than that of weak-base sulfide [(NH<sub>4</sub>)<sub>2</sub>S].

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