# ALUMINIUM NANOPOWDER APPLICATION IN HIGH-TEMPERATURE SYNTHESIS OF GALLIUM NITRIDE

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**Abstract**

A large amount of microelectronic devices components are based on the unique properties of gallium nitride. Our purpose was to find the most effective and simple way for gallium nitride (GaN) nanoparticles synthesis. GaN nanoparticles were prepared by a gallium oxide powder - aluminium nanopowder (NP) mixture combustion process under air atmosphere and with the use of calorimetric bomb (under nitrogen atmosphere, P = 0.3 MPa). The aluminium nanopowder was obtained by electrical explosion process of aluminium wire in argon atmosphere. The GaN nanoparticles synthesis is based on the high - temperature chemical binding of nitrogen in the presence of oxygen impurities, which leads to the formation of stable crystal nitrides phases: AlN, GaN. The combustion process includes two stages, the first one (low - temperature) caused an absorption hydrogen burning (800 - 1200 °C), the second stage (high - temperature) leads to nitrides formation (2000 - 2400 °C).

**Keywords:** Aluminium nanopowder, gallium nitride

## 1. INTRODUCTION

A large amount of microelectronic devices components are based on the unique properties of gallium nitride. For example, the gallium nitride Light Emission Diodes could be used for the conversion of electrical energy into light energy with efficiency up to 45% [1]. At the same time, the gallium nitride preparation involves technical difficulties, thus, the most simple and effective ways for the gallium nitride preparation need to be found.

The gallium nitride (GaN) is a direct bandgap semiconductor, the value of Eg is in the range of 3.25 -3.60 eV [2]. Gallium nitride powder is stable in acidic and alcaline solutions, GaN decomposes to the gallium oxide under air conditions (800 °C). GaN decomposition temperature is about 850 °C.

Our purpose was to find the most effective and simple way for the gallium nitride synthesis. There are a lot of techniques for the GaN preparation: 1) The conversion of metallic Ga in a $NH_3$ stream into GaN (1200°C); 2) the decomposition of $(NH_4)_3GaF_6$, $(GaCl{\cdot}NH_3)$ in a $NH_3$ stream (900 °C); 3) the nitriding of gallium. But there are some difficulties in the nitriding method related to a melt mirror formation of the low-melting-point gallium. This process leads to a response surface decrease and reaction rate decrease. In order to prevent this special agents, such as $(NH_2)_2CO_3$ are widely used. The agents decompose into gases, which mix the gallium melt and enable a nitrogen penetration to the gallium; 4) the gallium oxide reduction with nitriding process: $Ga_2O_3+2NH_3=2GaN+3H_2O$ (1100 -1200°C) [3].

It was reported about the gallium nitride preparation by a gallium oxide powder - aluminium nanopowder (NP) mixture combustion process under air atmosphere [4]. Gallium oxide and aluminium NP were mixed together, with that the powder mixture combustion process was initiated. This reaction was provided under air atmosphere as self-sustained process, which led to the gallium nitride formation. Afterwards the gallium nitride precipitation was provided with a sulfuric acid or a chlorohydric acid solution chemical treatment.

This method includes a great number of advantages, such as the usage of air nitrogen, the atmosphere pressure and the usage of the heat energy of chemical reactions for the gallium nitride synthesis. However, there are some disadvantages of the method, for example, low reaction product efficiency and the usage of porous structures, which are the inertial material in production.

The GaN synthesis is based on the high - temperature chemical binding of air nitrogen in the presence of oxygen, that leads to the formation of stable crystal nitrides phases. The combustion process includes two stages [5], the first one (low - temperature) caused an absorption hydrogen burning (800 - 1200 °C), the second stage (high - temperature) leads to nitrides formation (2000 - 2400 °C). Currently, the full mechanism of this phenomena has not been studied yet, but there is some evidence about a photochemical deactivation of oxygen during the nitride formation. Oxygen transferred the triplet state in the singlet inactive state. The reactivity of nitrogen after a heat increased and it's interacted with aluminium and formed aluminium nitride [6]:

$$O_2(^3\Sigma_g^-) + nhv \rightarrow O_2(^1\Delta_g^-) \quad (1)$$

$$N \equiv N + M^+M^- \rightarrow \left[N \equiv N\Lambda\ M^+M^-\right] \rightarrow 2M^+N^-. \quad (2)$$

It was reported about Nb [7], Ta [8], B, C [9], Al [6] and other elements nitrides formation.

## 2. EXPERIMENTAL PART

### 2.1. Synthesis via air condition

The aluminium nanopowder obtained by electrical explosion process under argon atmosphere was used to prepare metallic gallium - aluminium nanopowder mixture. Afterwards, the mixture was heated to 30-35 °C and mechanically mixed. In experiments the mixtures with next weight relations of the substances: Ga - Al 2:4, 3:3, 5:1. The combustion of freely poured mixtures was conducted in a box on the steel plate under free air conditions. The process of a combustion for the samples with the Ga - Al weight relations 2:4, 3:3 was provided as one - stage process, and for the samples with the Ga - Al weight relations 4:2 was provided as two - stage process. The combustion of the sample with Ga - Al weight relations 5:1 was weak, pointlike mostly.

AlN was prepared from Al nanopowder according to the following reaction:

$$2Al(NP) + N_2 \rightarrow 2AlN. \quad (3)$$

.

Combustion process was initiated by local heating of Al nanopowder sample using nichrome wire. The amounts of voltage and current applying were 15 V and 2 A respectively. The combustion process continued for 2 minutes after the initiation. After the reaction ending the sample was cooled in air atmosphere.

GaN was supposed to be prepare from the mixture of Al nanopowder and $Ga_2O_3$ according to the reaction:

$$2Al(NP) + Ga_2O_3 \rightarrow 2Al_2O_3 + 2Ga, \quad (4)$$

.

$$2Ga + N_2 \rightarrow 2GaN. \quad (5)$$

The $Ga_2O_3$ sample was prepared for the experiment by being passed through a sieve with a mesh of $mm^2$. After that Al nanopowder and $Ga_2O_3$ were mixed thoroughly. The combustion process of the mixture was described above.

### 2.2. Synthesis in calorimetric bomb

Synthesis via air and $N_2$ atmospheres was provided in calorimetric bomb under the pressure of 0.7 MPa according to the **Figure 1**. For the experiment GaN was prepared both with the additional amount of $NaN_3$ and without the one.

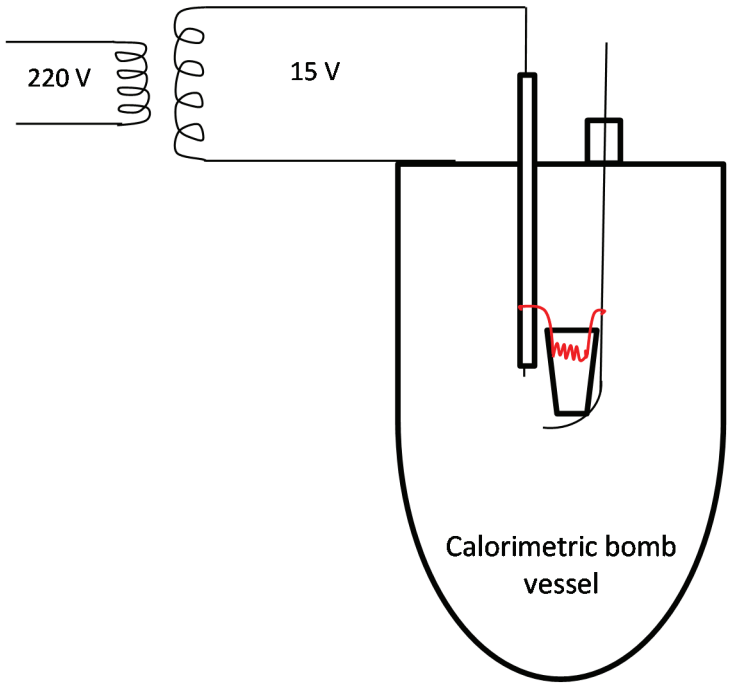


**Figure 1** The scheme of combustion synthesis in calorimetric bomb

### 2.3. TGA and DSC analyses

TGA and DSC analyses results are indicated in **Figure 2**. The analysis was conducted from 40 °C to 1200 °C in increments of 10 °C/min under air atmosphere. According to the thermograph a mass reduction occurred up to 470 °C with a following mass increasing up to 500 °C. After a slow oxidation stage (600°C - 735 °C) the second stage occurred up to 950 °C. Thus, the oxidation (combustion) process of the mixture with a ratio 2:2 included 2 stages, the same was observed for the aluminium nanopowder without an additive component. The feature of the process was desorption revealed at the first heating stage (3.3781 wt.%).

### 2.4. XRD analysis

The XRD patterns show that the formation of AlN via intermediate states takes place. The XRD of the AlN powder synthesized via air condition shows 4 stable phases (AlN, Al, $Al_2O_3$ and $Al_3O_3N$) whereas the products synthesized in calorimetric bomb show only 3 stable phases (AlN, Al and $Al_3O_3N$). According to the XRD data of Al nanopowder combustion products the process of chemical binding of air nitrogen takes place when $O_2$ is deactivated.

The XRD patterns of GaN synthesized in calorimetric bomb reveal that metallic Ga formation takes place and there are no clear reflexes of GaN. But the analysis shows that there are 3 unidentified reflexes that could be related to GaN formation.

The XRD analysis of combustion products with additional amount of $NaN_3$ shows pyrophoric Na metal.

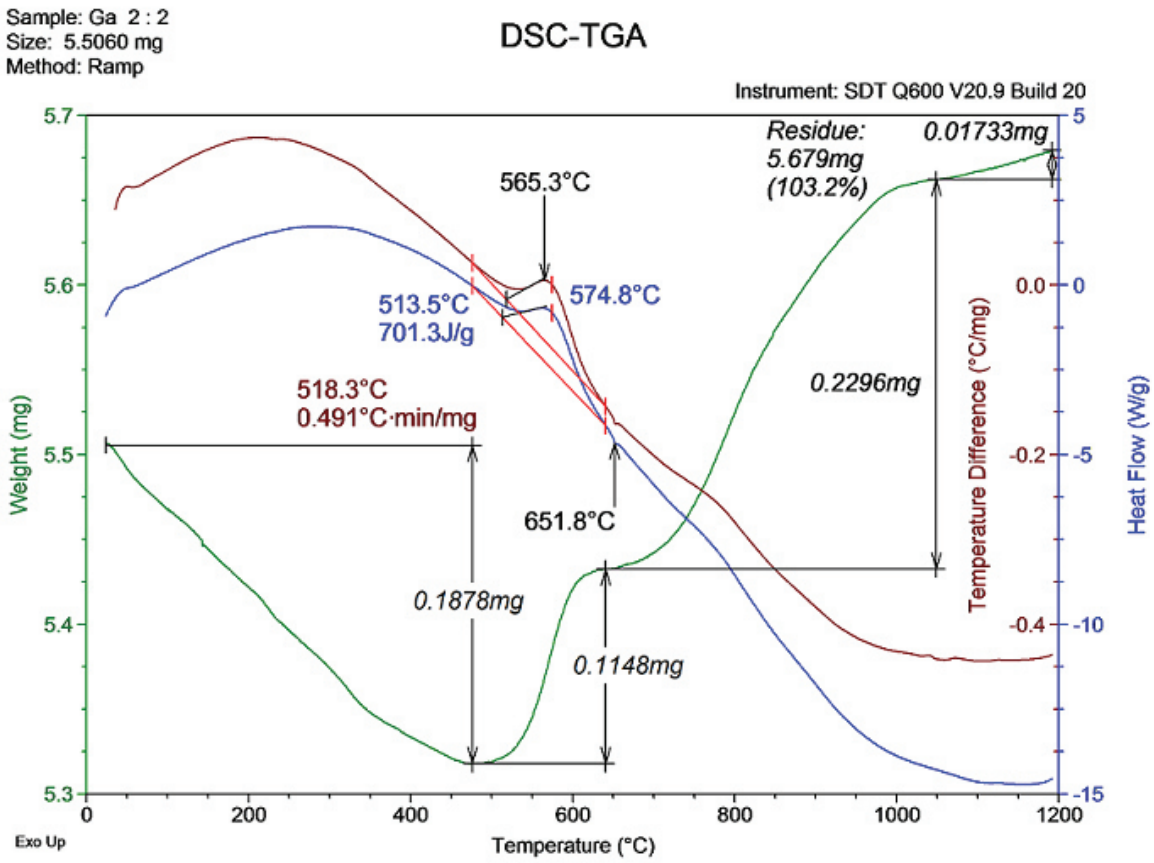


**Figure 2** TGA - DSC of gallium oxide powder - aluminium nanopowder (NP) mixture (2:2) (m=5.5060 mg, heat flow - 10 °C/min, air atmosphere)

## 3. CONCLUSION

GaN is a promising material due to its unique properties for a lot of areas, such as optoelectronics, military industry, space industry and biomedical technology [10]. Currently, a large amount of gallium nitride preparation methods are based on the reaction between ammonia and gallium component. But an application of this methods for big - scale production is obstructed by its high energy capacity and process time. The high - temperature chemical binding of an air nitrogen in the presence of oxygen is a very promising method of gallium nitride synthesis. The main advantages of high - temperature chemical binding process are short process time and low energy capacity. At the same time there are some difficulties related to the pure GaN, but the investigation in obtaining of the pure GaN are currently underway, because Ga is used in the GaN synthesis and as the substrate for the transfer of a γ - emitter in nuclear reactors.

According to the XRD data of Al nanopowder combustion products the process of chemical binding of air nitrogen takes place when $O_2$ is deactivated. It was founded AlN, Ga metal and $Al_2O_3$ (corundum) phases as products of Al(NP) - $Ga_2O_3$ mixture combustion (P=0.7 MPa).

$NaN_3$ was added to the samples for increasing of pressure in calorimetric bomb, pyrophoric Na metal was produced. But there are 3 unidentified reflexes from XRD analysis which could be GaN phase.

## ACKNOWLEDGEMENTS

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