

PAPER • OPEN ACCESS

# Temperature optimization of the Ti/Al/Ni/Au ohmic contact formation to the AlGaN/GaN heterostructure

To cite this article: S A Shostachenko *et al* 2017 *J. Phys.: Conf. Ser.* **938** 012072

View the [article online](#) for updates and enhancements.

## Related content

- [Influence of dislocations in the GaN layer on the electrical properties of an AlGaN/GaN heterostructure](#)  
Gao Zhi-Yuan, Hao Yue, Zhang Jin-Cheng et al.
- [Fabrication of an InAlN/AlGaN/AlN/GaN Heterostructure with a Flat Surface and High Electron Mobility](#)  
Masanobu Hiroki, Narihiko Maeda and Takashi Kobayashi
- [Percolation transport in an AlGaN/GaN heterostructure](#)  
N Sawaki, X X Han, Y Honda et al.

# Temperature optimization of the Ti/Al/Ni/Au ohmic contact formation to the AlGaN/GaN heterostructure

S A Shostachenko<sup>\*1</sup>, Y A Porokhonko<sup>1</sup>, R V Zakharchenko<sup>1</sup>, M S Burdykin<sup>1</sup>, R V Ryzhuk<sup>1</sup>, N I Kargin<sup>1</sup>, B V Kalinin<sup>2</sup>, A A Belov<sup>2</sup> and A N Vasiliev<sup>2</sup>

<sup>1</sup>National Research Nuclear University MEPhI, Moscow, Russian Federation

<sup>2</sup>PLANETA-IRMIS, Saint Petersburg, Russian Federation

E-mail: Sashostachenko@mephi.ru

**Abstract.** This article is devoted to the experimental study of the ohmic contacts based on Ti/Al/Ni/Au metallization to the n+-doped region of the AlGaN / GaN heterostructure. Formed phases are studied at different temperatures. Based on the thermodynamic analysis of possible intermetallic reactions in the contact region, the optimum temperature range was found for the formation of ohmic contacts with a low contact resistance. The optimality of the modeled range is experimentally confirmed.

## 1. Introduction

Transistor devices based on III-nitride heterostructures are widely used both in the defense and civilian industries. For example, as the main component of microwave monolithic integrated circuits (microwave MIS) millimeter and submillimeter bands for communication systems, radiolocation, radio astronomy, radiometry, etc. [1], these materials, especially GaN, have also been used in the optoelectronic industry as a base for LED crystals.

In such devices ohmic contacts with a low contact resistance play an important role. To form such contacts to heterostructures based on GaN n-type conductivity, multilayer contacts based on Ti / Al.

The ohmic contact formation mechanisms on the basis of the Ti/Al metal system during thermal annealing are based on the appearance of a  $Ti_xN$  compound with a metallic type of conductivity.  $Ti_xN$  begins to form even when the titanium is deposited on the n-GaN surface and propagates in the bulk of the titanium metallization layer during thermal annealing. The formation of the  $Ti_xN$  layer makes nitrogen vacancies concentration in gallium nitride to increase near the TiN-GaN interface. These vacancies are donor levels that dramatically increase the electrical conductivity of an n-type semiconductor, which is one of the reasons for the low contact resistance [2]. In addition, Ti/Al-based metallization reduces the contact resistance by forming intermetallic compounds with a low work function on the GaN surface [3-7]. Needed intermetallic compounds are formed in the contact system during "rapid" annealing at high temperatures because of chemical reactions of the elements in the contact system.

Nitrides, intermetallides and free titanium and aluminum are present among the products of interaction. It sufficiently complicates the stability analysis of the Al/Ti/GaN contacts, which requires patterns detection of solid-phase reactions between contacting materials and changes in the phase composition of these structures in the temperature range of contact formation and their operation.



It is important to determine the optimum annealing temperature to form ohmic contacts with a low contact resistance. In this paper, this is done with help of the thermodynamic analysis. The results are confirmed by X-ray diffraction analysis of the obtained samples and experimentally obtained temperature dependence of the contact resistance.

## 2. Experimental method

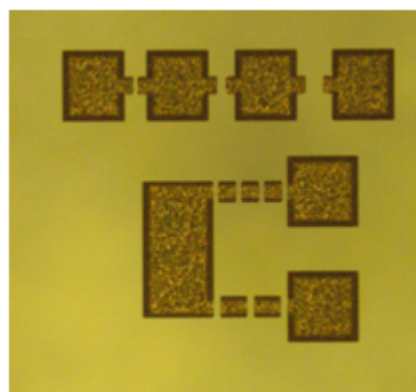
In this work we used a substrate with an AlGa<sub>x</sub>N/GaN heterostructure. Electron concentration in the upper AlGa<sub>x</sub>N layer was  $3 \times 10^{18} \text{ cm}^{-3}$ . The schematic profile of the heterostructure is shown in Fig. 1.

The surface was chemically treated in a mixture of NH<sub>4</sub>OH: H<sub>2</sub>O (DI) (1:10) before the metallization process to reduce the value of the contact resistance of the contacts [8].

Four-layer metallization of Ti/Al/Ni/Au (35/135/50/100 nm) was applied to the surface of the heterostructure by the resistive sputtering method in the Kurt J. Lesker PVD 75 [8]. The parameters of the ohmic contacts were measured by the long line method (TLM) [9]. The test structures (shown in Fig. 2) were manufactured to increase the accuracy of measuring the resistance of ohmic contacts [10]. The desired contact metallization pattern was created by inverse photolithography. Then the samples underwent rapid thermal annealing at the Modular RTP-600S unit at a given temperature for 30 seconds. Specific contact resistance was measured on an analyzer of Agilent B 1500 A semiconductor devices.

Сар-слой GaN, 2.5 нм
n <sup>+</sup> - Al <sub>x</sub> Ga <sub>1-x</sub> N (x <sub>Al</sub> =26%) легированный Si (N <sub>d</sub> =3×10 <sup>18</sup> ), 13 нм
Спейсер, Al <sub>x</sub> Ga <sub>1-x</sub> N, 2.0 нм
AlN 1.3 нм
GaN 2500 нм
Сапфир 430 мкм

**Figure 1.** AlGa<sub>x</sub>N/GaN heterostructure



**Figure 2.** Test module for ohmic contacts resistance determination

An X-ray diffractometer Ultima IV was used to study the changes in the phase composition of the contact region, due to the appearance of intermetallic compounds of titanium, nitrogen and aluminum at different annealing temperatures.

## 3. Thermodynamic analysis of the Al-Ti-N system

Thermal treatment of Al/Ti/GaN structures is accompanied by the diffusion of nitrogen atoms, which interact with metal atoms in the temperature range 800-1000°C. Atoms form solid interstitial solutions and chemical compounds of nitride (AlN, TiN, Ti<sub>2</sub>N), and in addition, during the interaction of titanium with aluminum compounds are formed by Al-Ti (AlTi, AlTi<sub>3</sub>, Al<sub>3</sub>Ti, Al<sub>2</sub>Ti, Al<sub>3</sub>Ti<sub>2</sub>). The phase diagrams of possible binary systems from the initial three elements: aluminum, titanium and nitrogen, were studied in details in work [11].

To analyze the probability of occurrence and stability of these phases, it is necessary to take into account all possible chemical interactions of the initial three elements and for each reaction to calculate the temperature dependence of the change in the free Gibbs energy of the solid-phase reactions of formation of each compound and its temperature dependence. Phases are formed and are

thermodynamically stable if the change in the free Gibbs energy (isobaric-isothermal potential)  $\Delta G < 0$  in the considered temperature range for all reactions. To calculate this value, use the formula 1 [11-12]:

$$\Delta G(T) = \Delta H_{298}^0 - T\Delta S_{298}^0 + \int_{298}^T \Delta c_p(T) dT - T \int_{298}^T \left( \frac{\Delta c_p(T)}{T} \right) dT, \quad (1)$$

where  $\Delta G(T)$  – change in Gibbs energy of the reaction;  $\Delta H_{298}^0$  – change in enthalpy of reaction under standard conditions;  $\Delta S_{298}^0$  – change in the entropy of the reaction under standard conditions;  $\Delta c_p(T)$  – change in the heat capacity of the reaction, T – temperature in Kelvin.

In carrying out further calculations, reference data were used on the thermodynamic properties of elements, their nitrides and intermetallic compounds [13-15]. However, the properties of many compounds are not reflected in these sources. In this case, calculations were made using the thermodynamic properties of the compounds elements. The accuracy and limits of applicability of various calculation methods have been studied in sufficient detail in works [11-12, 16-17]. An analysis of various methods for calculating the thermodynamic properties of substances made it possible to conclude that the Neumann-Kopp method, which uses the rule of additivity of the thermodynamic properties of elements in the formation of a condensed binary compound, is the optimal method to ensure an acceptable accuracy of calculations [15]. As a result, the heat capacity of compound  $A_qB_r$  is determined by the formula:

$$C_{p,A_qB_r} = K_{NK}(qC_{p,A} + rC_{p,B}) \quad (2)$$

where  $K_{NK}$  – coefficient reflecting the deviation from the Neumann-Kopp rule.

Precisely the value of the  $K_{NK}$  coefficient can be determined using the Kelly rule, according to which, the heat capacity of the compound is determined by the expression 3 at the melting point or the first polymorphic transformation [18]:

$$C_p(T_{пл}) = K_K m \quad (3)$$

where m – number of atoms in the molecule of the compound;  $K_K = 29,3$ .

Then the expression for determining the coefficient  $K_{NK}$  can be written in the form:

$$K_{NK} = \frac{K_K(q+r)}{(qC_{p,A}(T_{пл}) + rC_{p,B}(T_{пл}))} \quad (4)$$

Using expressions (2) and (4), we can determine the temperature dependence of the specific heat of the compounds, using the reference data for the specific heat of the components and the values of their melting points and polymorphic transformations [15, 20].

It should be noted that at temperatures below 882°C, titanium has  $\alpha$ -Ti modification with a hexagonal close-packed lattice, at temperatures above 882°C,  $\beta$ -Ti with a cubic body-centered lattice. [11] Consequently, the thermodynamic functions of titanium before and after 882°C are different. As a result, for some compounds it is necessary to separately consider the temperature ranges before and after 882°C.

As a result of calculations, it was revealed that the general form of the free Gibbs energy dependence on temperature is of the following character:

$$\Delta G = a + b \cdot T + \frac{c}{T} + d \cdot T^{\frac{3}{2}} + e \cdot T^2 + f \cdot T^3 + g \cdot T \cdot \ln T, \quad (5)$$

where T – temperature in Kelvins; a, b, c, d, e, f, g – approximating coefficients.

Table 1 presents the values of the approximating coefficients for various compounds at temperatures below 882°C, and in Table 2 at temperatures above 882°C.

**Table 1.** Values of coefficients at temperature up to 882°C

	a	b	c	d	e	f	g
TiN	$-3.36 \cdot 10^5$	92.9	0	0	0	0	0
AlTi	$7.22 \cdot 10^5$	$-7.52 \cdot 10^2$	$-3.66 \cdot 10^4$	27.1	$44.8 \cdot 10^{-5}$	0	7.62
Al <sub>3</sub> Ti	$-4.12 \cdot 10^4$	$-1.09 \cdot 10^3$	$-5.32 \cdot 10^4$	39.4	$62.9 \cdot 10^{-5}$	0	11.1
AlTi <sub>3</sub>	0	$9.07 \cdot 10^2$	$-4.25 \cdot 10^4$	-47.3	$-10.1 \cdot 10^{-4}$	0	-15.8
Ti <sub>2</sub> Al <sub>3</sub>	$-1.33 \cdot 10^9$	$3.02 \cdot 10^6$	$-1.12 \cdot 10^5$	177	$-46.4 \cdot 10^{-5}$	0	$-4.52 \cdot 10^5$
Al <sub>2</sub> Ti	$2.82 \cdot 10^3$	$-4.57 \cdot 10^2$	$-3.12 \cdot 10^4$	15.8	$7.66 \cdot 10^{-5}$	0	7.17
AlN	$-3.22 \cdot 10^5$	93.3	0	0	0	0	0

**Table 2.** The values of the coefficients at the temperature after 882°C

	a	b	c	d	e	f	g
TiN	$-3.38 \cdot 10^6$	95.3	0	0	0	0	0
AlTi	$-7.10 \cdot 10^4$	-90.3	$-2.99 \cdot 10^4$	0	$57 \cdot 10^{-5}$	0	13.4
Al <sub>3</sub> Ti	$-1.73 \cdot 10^5$	551	$2.48 \cdot 10^4$	0	$3.87 \cdot 10^{-3}$	0	-82
AlTi <sub>3</sub>	$-7.81 \cdot 10^4$	-129	$-1.99 \cdot 10^4$	0	$38 \cdot 10^{-5}$	0	15.8
Ti <sub>2</sub> Al <sub>3</sub>	$-9.78 \cdot 10^9$	-116	$-3.58 \cdot 10^4$	0	$6.2 \cdot 10^{-5}$	0	13.9
Al <sub>2</sub> Ti	0	52.2	$-1.99 \cdot 10^4$	0	$27.7 \cdot 10^{-5}$	0	-7.17
AlN	$-3.22 \cdot 10^5$	93.3	0	0	0	0	0

The results of calculating the change in the free Gibbs energy for the temperatures and compounds of interest to us are presented in Table 3.

**Table 3.** The calculated free Gibbs energy of the reactions of formation of double compounds at different temperatures.

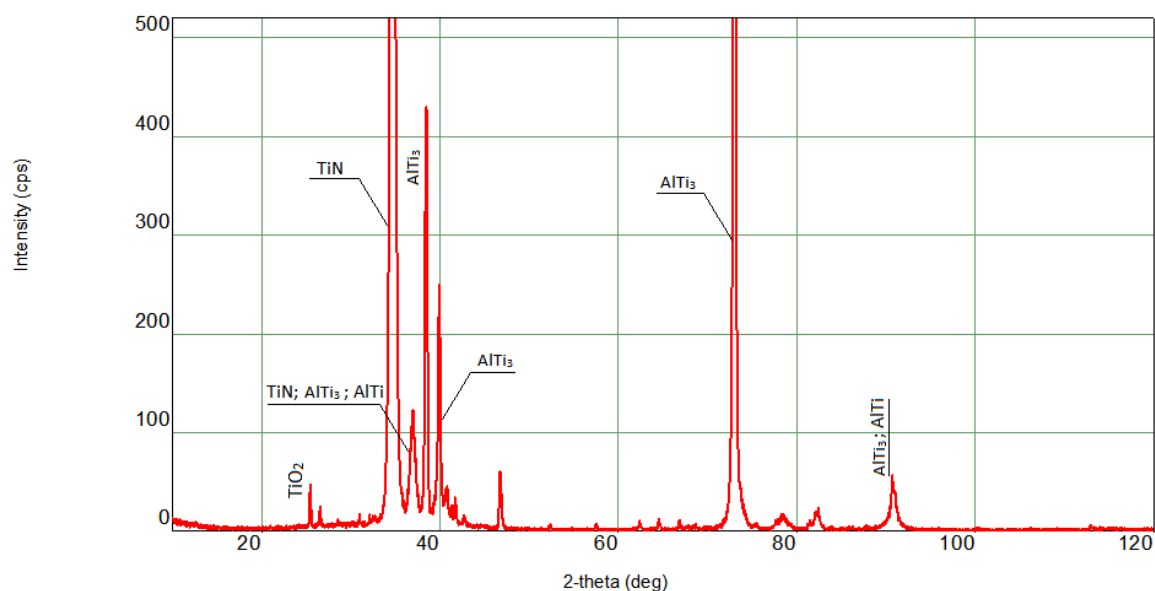
Reaction	$\Delta G$ , kJ/mol					
	800°C	850°C	880°C	900°C	950°C	1000°C
1. Ti+N=TiN	-238	-231	-229	-226	-222	-217
2. Al+Ti=AlTi	1080	1150	1190	-64.3	-63.2	-62.1

3. $3\text{Al}+\text{Ti}=\text{Al}_3\text{Ti}$	254	302	331	-128	-126	-124
4. $3\text{Ti}+\text{Al}=\text{AlTi}_3$	-810	-889	-398	-98.0	-97.9	-97.8
5. $2\text{Ti}+3\text{Al}=\text{Al}_3\text{Ti}_2$	1650	1860	1910	-117	-117	-116
6. $\text{Al}+\text{N}=\text{AlN}$	-206	-200	-197	-194	-188	-183
7. $\text{Ti}+2\text{Al}=\text{Al}_2\text{Ti}$	121	141	152	-9.61	-0.761	-1.37

The reaction of formation of a given compound is thermodynamically probable for  $\Delta G < 0$ . Moreover, the reaction is thermodynamically more probable, in which  $\Delta G$  is smaller. As can be seen from Table 3, the free energy of formation of all possible titanium aluminides, except  $\text{AlTi}_3$  aluminide, is less than zero only at 900°C and above, hence, as indicated above, they appear and remain thermodynamically stable at these temperatures. Aluminide  $\text{AlTi}_3$  and nitrides  $\text{AlN}$  and  $\text{TiN}$  nitrides appear and are stable even at 800°C.

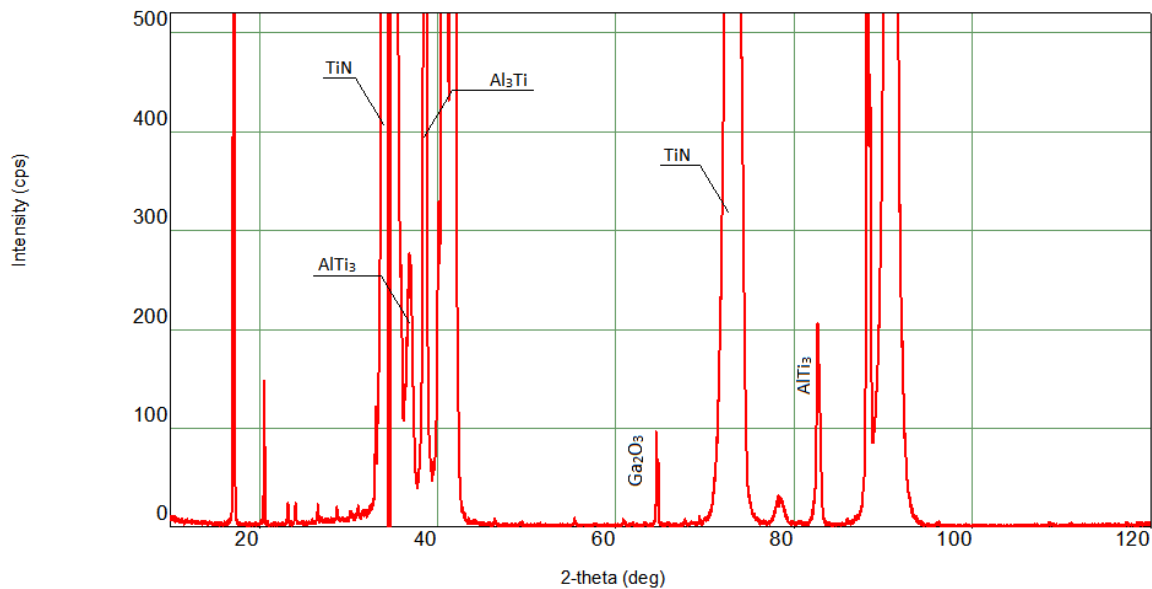
#### 4. Results and discussion

An x-ray diffraction analysis of the experimental samples was carried out to confirm the results of the above thermodynamic analysis. The results are shown in Fig. 6-8. After annealing at a temperature of 800°C, the presence of the following main phases was found:  $\text{TiN}$ ,  $\text{AlTi}_3$  (Fig. 3), which coincides with the calculated results (Table 3). Also a small peak is found on the roentgenogram, which is the titanium oxide formed by the interaction of the deposited titanium with the residuals of gallium oxide.



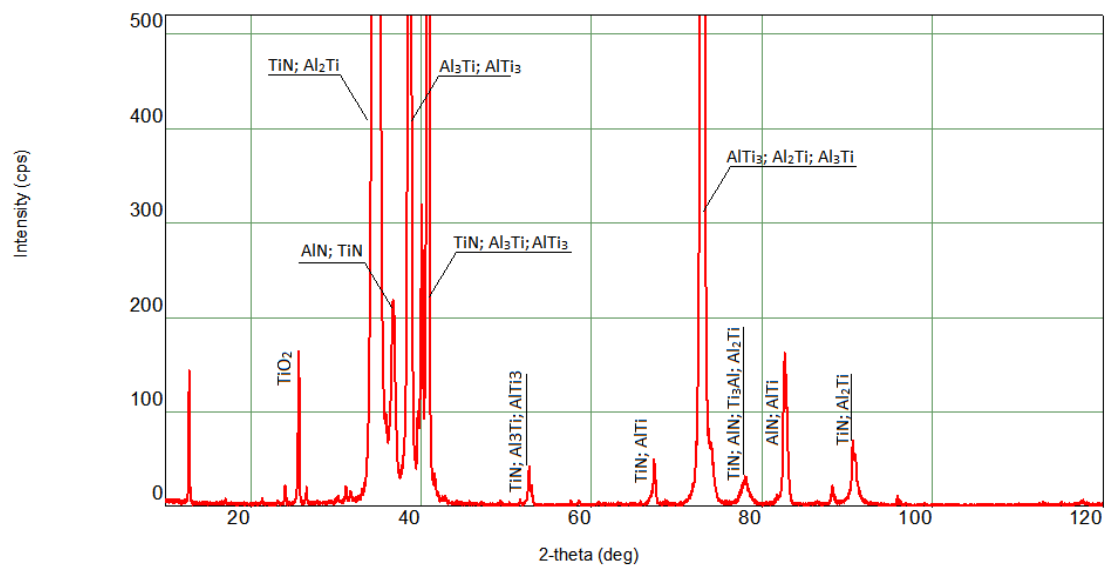
**Figure 3.** The X-ray diffraction pattern of the sample after annealing at 800°C

After annealing at 850°C (Fig. 4), the same phases were detected as in the case of 800 °C, but the height of the peaks indicates increasing in the content of TiN. Also, a low peak was found which corresponds to the residue of oxides  $\text{Ga}_2\text{O}_3$ .



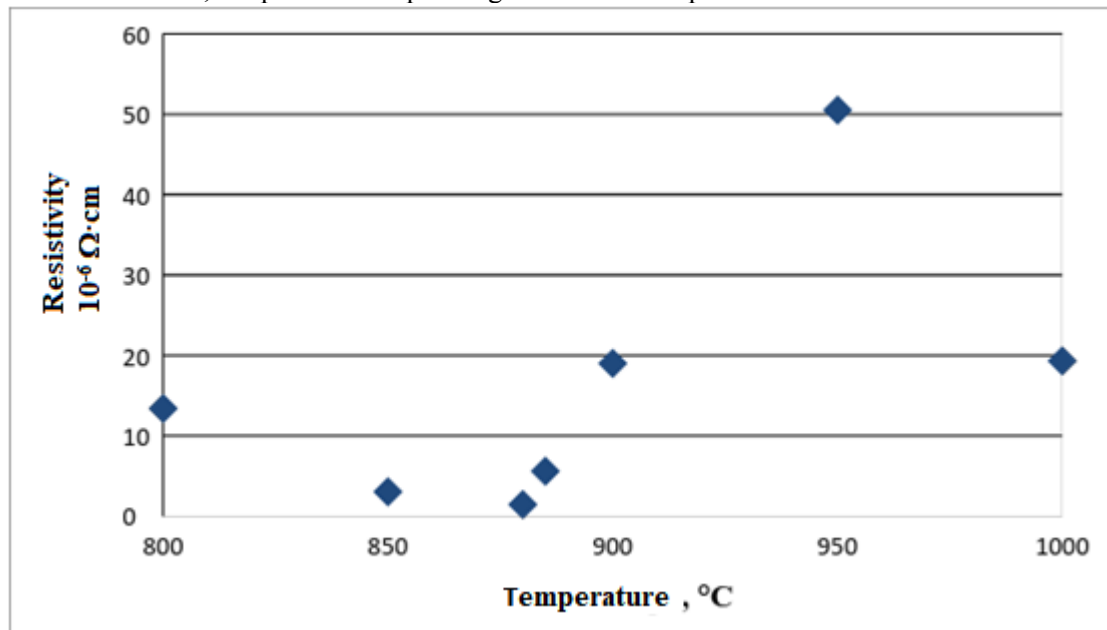
**Figure 4.** The X-ray diffraction pattern of the sample after annealing at 850°C

After annealing at 900°C, a greater number of phases are formed: AlN, TiN, AlTi<sub>3</sub>, AlTi, Al<sub>2</sub>Ti, Al<sub>3</sub>Ti (fig.5), i.e. aluminides (Al<sub>2</sub>Ti, AlTi и AlN) are formed additionally, which is also coincides with the thermodynamic calculations. The appearance of aluminum nitride, which is a dielectric, can increase the contact resistance. The peak corresponding to the titanium oxide was found again.



**Figure 5.** The X-ray diffraction pattern of the sample after annealing at 900°C.

Thus, at temperatures of 850°C and lower, as expected, less aluminum and titanium aluminide is formed, and as a result, the formation of a TiN compound and the corresponding amount of nitrogen vacancies in the semiconductor is more likely. When the annealing temperature changes from 800°C to 850°C, the peaks corresponding to the TiN compound increase.



**Figure 6.** Specific contact resistance after annealing

Thus, we can expect that the optimal temperature conditions for the formation of the ohmic contacts are temperatures from 850 to 900°C, since free titanium is used to form fewer different aluminides, which follows from the data presented in Table 3. This increases the probability of the formation of titanium nitride, which is accompanied by the formation of nitrogen vacancies in the contact region of GaN. These vacancies create donor levels, due to which there is an increase in the n-type conductivity in the contact area and a decrease in the contact resistance.



Data on the phase composition of the contact region (Fig. 3-5) were compared with data on the contact resistance (Fig. 6). As expected, the minimum resistance is observed at an annealing temperature of 850 to 900 °C. That is, experimentally confirmed the assumption made on the basis of thermodynamic calculations for possible intermetallic reactions in the contact region. In this temperature range, the probability of TiN compound formation is higher, and titanium aluminides are lower than at higher temperatures.

## 5. Conclusion

In this paper we analyzed the effect of solid-state interaction processes in Al/Ti/GaN contacts during heat treatment on their final structure and electrical parameters. The analysis showed that after annealing the contact area is transformed into a structure that consists of phases that are the products of solid-phase interaction of three basic elements: titanium, nitrogen and aluminum.

As a result of the analysis of the thermodynamics of the reactions interaction of the three basic elements, it has been established that the optimal temperature range for the formation of good ohmic contacts is 850-900 °C. In this temperature range, the probability of formation of TiN compound is higher, and the aluminides of titanium and aluminum nitride are lower than at higher temperatures. This was confirmed by the results of direct measurements: the value of the specific contact resistance of the contact was  $1.44 \cdot 10^{-6} \Omega \cdot \text{cm}^2$ , which is lower than the values obtained in similar studies [18-21].

The presented approach is also valid for samples whose upper layer consists of an AlGaN ternary semiconductor with a Ti/Al-based metallization system applied to it, since the fast annealing contacts contain the same elements as when annealing contacts to a heterostructure with an upper GaN layer.

## Acknowledgements

## References

- [1] Luther B P and Mohny S E 1997 Investigation of the mechanism for Ohmic contact formation in Al and Ti/Al contacts to n-type GaN *Appl. Phys. Lett.* V 70 P 57
- [2] Schubert E F 2003 Light-emitting diodes *Cambridge University Press*
- [3] Kong X, Wei K, Liu G and Liu X 2012 Role of Ti/Al relative thickness in the formation mechanism of Ti/Al/Ni/Au Ohmic contacts to AlGaN/GaN heterostructures *J. Phys. D: Appl. Phys.* V 45 P 265101
- [4] Durbha, Pearton S J, Abernathy C R, Lee J W and Holloway P H 1996 Microstructural stability of ohmic contacts to  $\text{In}_x\text{Ga}_{1-x}\text{N}$  *J. Vac. Sci. Tech B* V 14 P 2582
- [5] Morkoc H, Strike S, Gao G B, Lin M E, Sverdlov B and Burns M 1994 Large- band- gap SiC, III- V nitride, and II- VI ZnSe- based semiconductor device technologies *J. Appl. Phys.* V 76 P 1363
- [6] Vanyukhin et al 2013 Investigation of the structure and morphology of the surface of a two-layer Ti / Al contact metallization *Proceedings of universities. Materials of electronic engineering(in Russian)* №3 p 60-65
- [7] Vanyukhin K D et al 2016 Study of structure and surface morphology of two-layer contact Ti/Al metallization *Modern Electronic Materials (MOEM)* T 2 №2 p 54–59
- [8] Lester F, Brown J M, Raner J C and Zhang L 1996 Nonalloyed Ti/Al ohmic contacts to n-type GaN using high-temperature premetallization anneal *Appl. Phys. Lett.* V 69 №18 pp 2737-2739
- [9] Reeves G., Harrison H. B. Obtaining the specific contact resistance from transmission line model measurements // *IEEE Electr. Device Lett.* 1982 V. 3. P. 111.

- [10] Shostachenko S 2015 Schottky-to-Ohmic Behavior in Annealed Ti/Si/Ti/Al/Ni/Au on AlGa<sub>N</sub>/Ga<sub>N</sub> *Physics Procedia* V 72 P 419
- [11] Tretyakov Y D 1978 Solid-phase reactions (in Russian) *Moscow: Chemistry* p 360
- [12] Kireyev V A 1975 Methods of Practical Calculations in Thermodynamics of Chemical Reactions (in Russian) *Moscow: Chemistry* p 536
- [13] Samsonov G V and Vinitskiy I M 1976 Refractory compounds (in Russian) *Moscow: Metallurgy* p 560
- [14] Chase M W Jr, Davies C A, Downey J R et al 1985 JANAF Thermochemical Tables. Third edition *J. Phys. Chem. Ref. Data* V 14 Suppl 1
- [15] Kubashevsky O and Alkock K B 1982 Metallurgical thermochemistry *Moscow: Metallurgy* p 392
- [16] Morachevsky A G and Sladkov I B 1993 Thermodynamic calculations in metallurgy *Moscow: Metallurgy* p 304
- [17] Moiseev G K and Sestak J 1995 Some calculations methods for estimation of thermodynamical and thermochemical properties of inorganic compounds *Prog. Crystal Growth and Characterization* vol 30 pp 23
- [18] Kong X, Wei K, Liu G and Liu X 2012 Role of Ti/Al relative thickness in the formation mechanism of Ti/Al/Ni/Au Ohmic contacts to AlGa<sub>N</sub>/Ga<sub>N</sub> heterostructures *J Phys. D: Appl. Phys.*
- [19] Xin H P et al 2010 *CS Mantech Conference* V45
- [20] Butteri et al 2002 Systematic characterization of Cl<sub>2</sub> reactive ion etching for improved ohmics in AlGa<sub>N</sub>/Ga<sub>N</sub> HEMTs *IEEE Electron Device Letters* V 23 P 76.
- [21] Jacobs B, Kramer M C J C M Geluk E J and Karouta F 2002 Optimisation of the Ti/Al/Ni/Au ohmic contact on AlGa<sub>N</sub>/Ga<sub>N</sub> FET structures *Journal of Crystal Growth* V 241 Issues 1–2 P 15