

# Investigation into the processes of atom redistribution encountered during of the formation of metal layers on the surface of aluminum gallium nitride

I A Lamkin<sup>1</sup>, S A Tarasov<sup>1</sup>, A A Petrov<sup>1</sup>, E A Menkovich<sup>1</sup>, A V Solomonov<sup>1</sup>, S Yu Kurin<sup>2</sup>

<sup>1</sup>Saint-Petersburg Electrotechnical University “LETI”, Prof. Popova 5, St. Petersburg 197376, Russia

<sup>2</sup>GaN-Crystals Ltd., 27 Engels Ave, St. Petersburg 194156, Russia,

E-mail: ialamkin@mail.ru

**Abstract.** The results of an investigation into the properties of double-layer metal contacts to the epitaxial layers of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  solid solutions for ultraviolet photodetectors and UHF electronic devices are presented. The processes of atom redistribution during the formation of metal layers and their subsequent annealing to form low resistance contacts were studied by Auger electron spectroscopy. The results obtained allowed us to develop a technique for creating ohmic contacts having low resistance value.

## 1. Introduction

The metal contacts play an important role in the operation of modern optoelectronic and UHF devices based on nitrides and other wide-bandgap semiconductors [1-3]. Atom redistribution during the formation of these layers, as well as further thermal effects, have a strong influence on the devices characteristics. The parameters of metal layers are of special importance for the creation of photodetectors based on Schottky barrier [4], allowing for the control of not only their electrical characteristics, but also the degree of selectivity of the spectral sensitivity. The current-voltage (I-V) characteristics and the contact resistance of metal-semiconductor (MS) structure strongly depend not only on the metal contact, but also on the processes occurring at the MS interface during the preparation of the epitaxial layer surface, metal deposition and subsequent high-temperature treatment [5].

Currently during the formation of ohmic contacts to gallium nitride (GaN) and aluminum gallium nitride solid solutions ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ) the technologies of vacuum thermal evaporation or electron beam-induced deposition of thin metal layers or multilayer metal compositions are used. Typically used metals are Ti [6], Al [7 - 9], Ti/Al [10, 11], Ti/Ag [12], Ti/Al/Ni/Au [13] with subsequent high-temperature annealing in nitrogen ( $\text{N}_2$ ) ambient [14, 15]. It was shown [13] that in four-layer contacts, e.g. Ti/Al/Ni/Au, Ni acts as a blocking layer that prevents diffusion of Au into Ti and Al layers. Such metal can be Ti, Ni, Mo or Pt [16]. Au top layer facilitates unwelding of gold contacts when attaching photosensitive chip to package contacts and also performs a protective function [14]. The best results in the formation of ohmic contacts to  $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}$  were achieved using double-layer Ti/Al contacts with subsequent “fast” (90 s) annealing in  $\text{N}_2$  ambient at high temperature of 800 - 900 °C [8], the resistance value was equal to  $10^{-4}$  ohm · cm<sup>2</sup>.

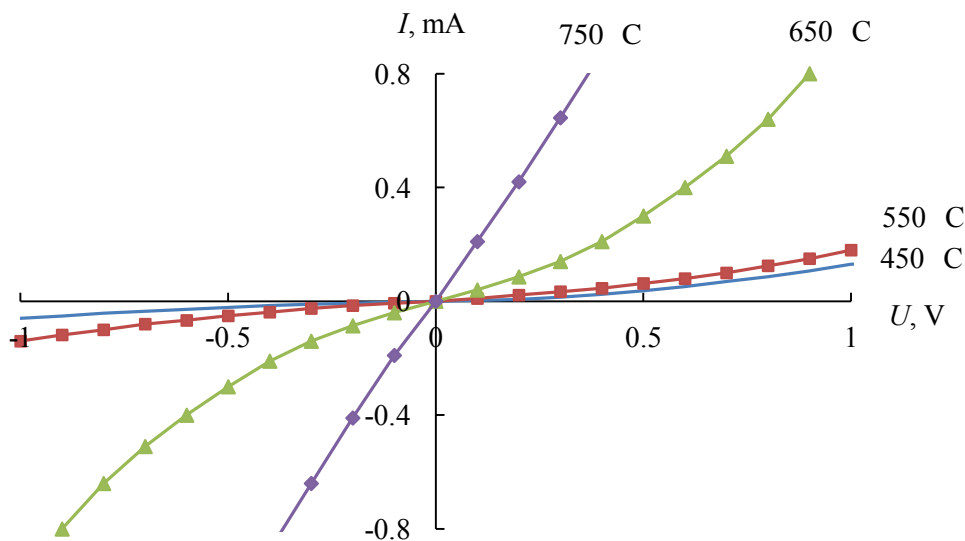


## 2. Sample and experimental technique

We investigated the samples grown by two approaches: molecular beam epitaxy with  $N_2$  plasma activation under metal-rich conditions and hydride vapor phase epitaxy [17] on c- $Al_2O_3$  substrates. The contacts were formed by vacuum thermal evaporation at pressure of residual gases of  $10^{-5}$  Torr. As structures Ti/Al double-layer compositions were created and studied. The thickness of metal layers was in the range of 15-75 nm. The best results were achieved for the Ti layer thickness of 15 nm, and the top Al layer thickness of 35 nm. Before deposition of the metal contacts to the surface, the structures were cleaned using various chemicals, in particular,  $H_2O_2$ ,  $CCl_4$ ,  $HCl$ , followed by structures washing in distilled water. For better metal adhesion the structures were heated to a temperature of  $300^\circ C$  during the deposition. To obtain ohmic I-V characteristics the contacts were annealed in vacuum at different residual gas pressures for 1-30 minutes.

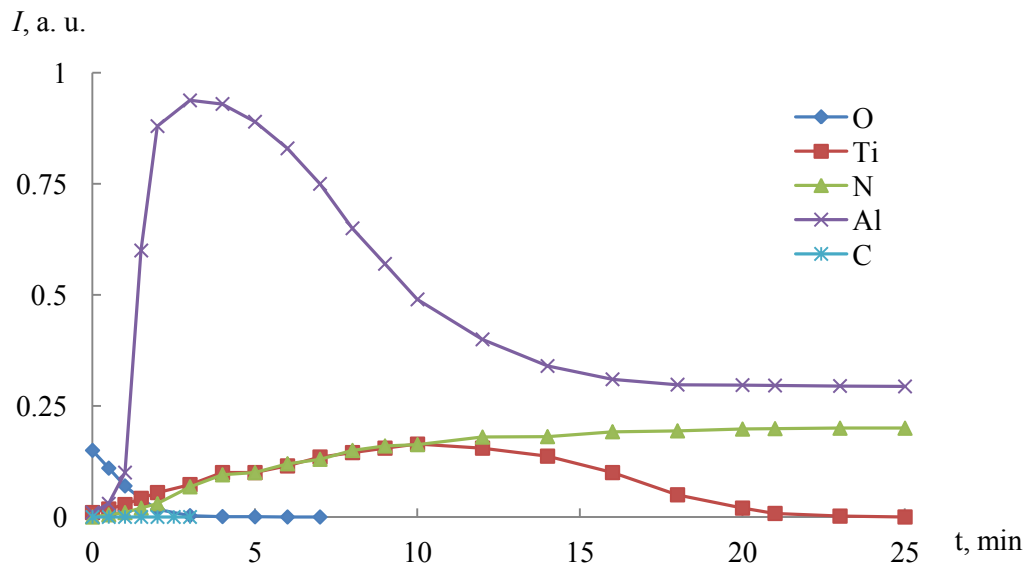
## 3. Experimental results and discussions

Figure 1 shows the I-V characteristics of the Ti/Al contacts to n-type  $Al_xGa_{1-x}N$  with aluminum content  $x = 0.08$ . One can see that the I-V characteristics of the contacts are non-linear both for untreated structures and structures annealed at relatively low temperatures. Nonlinearity decreases with the increase of temperature, and at  $750^\circ C$  contacts become ohmic. Further increase of the annealing temperature leads to a slight increase slope, but this increase is insignificant.



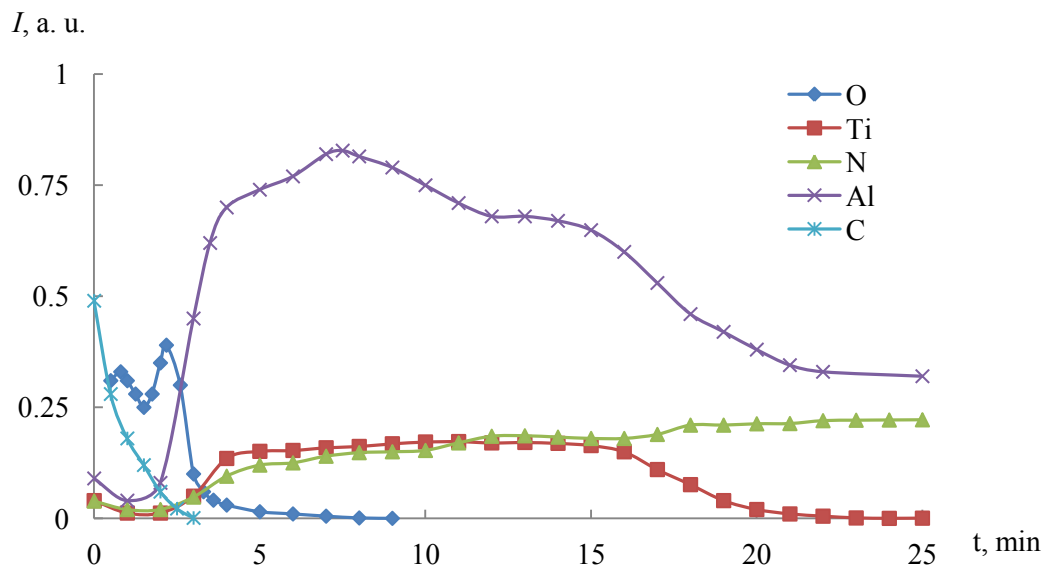
**Figure 1.** Current-voltage characteristics of the ohmic Ti / Al contacts to the  $Al_{0.08}Ga_{0.92}N$  layer annealed at the different temperatures for 10 minutes.

Several samples were investigated by Auger electron spectroscopy (AES) to study the distribution of metal atoms in the surface region of the ohmic contacts and the influence of high temperature annealing on this distribution. Figure 2 shows the Auger spectrum of the Al/Ti/ $Al_{0.5}Ga_{0.5}N$  structure after deposition of metals. One can see that although there is a small concentration of oxygen on the surface of the structure, its concentration is not high, and the penetration depth is very low. This may indicate high quality of the created structure. As well, the Al layer is also clearly visible on the graph; its thickness was originally equal to 35 nm. The sublayer for Al is a 15 nm thick titanium layer. However, the results of AES show that there is a partial mixing of titanium layer with aluminum top layer. Titanium also penetrates into the  $Al_{0.5}Ga_{0.5}N$  epitaxial layer.



**Figure 2.** AES depth profile of the structure Al/Ti/Al<sub>0.5</sub>Ga<sub>0.5</sub>N as deposited.

Figure 3 shows the AES-profile of the Al/Ti/Al<sub>0.5</sub>Ga<sub>0.5</sub>N structure after annealing for 10 min at 750 °C in vacuum at a residual gas pressure of  $10^{-5}$  Torr. One can see that both concentration and penetration depth of oxygen are increased, but still remain insufficient to affect the quality of the structure. The same is true for a small concentration of carbon.



**Figure 3.** AES depth profile of the structure Al/Ti/Al<sub>0.5</sub>Ga<sub>0.5</sub>N after annealing at 750 °C.

The important effect observed from the results of ASE in the annealed structures is a penetration of aluminum into the depth of the structure followed by nitrogen release from the surface region. As a result, profiles of N, Ti and Al in the top of the structure have almost the same depth. This may indicate the formation of titanium aluminum nitride composition that leads to improvement of ohmic I-V characteristics.

The analysis of investigated characteristics allowed us to formulate some conclusions on redistribution processes of atoms in the studied structures. In our opinion, during annealing there are two basic phenomena that determine the formation of ohmic contact. The first of them is a release of nitrogen by titanium from epitaxial layer [18]. Nitrogen diffuses actively into the metal layers resulting in relatively uniform distribution within. Titanium is also redistributed in the metal layer and the shape of its profile is similar to the profile of nitrogen (Fig. 4). This could indicate phase formation on the surface of semiconductor that is similar in composition to titanium nitride. Titanium does not penetrate into the depth of semiconductor interacting only with nitrogen. It is possible that a thin layer with a higher concentration of titanium and nitrogen is formed on the surface of semiconductor (some increase in the profile of both atoms for 15 s is observed). It is important that in this case nitrogen is removed from the near-surface layer of semiconductor that leads to the formation of nitrogen vacancies therein. Such vacancies behave as donors [19, 20]. Therefore, this process may be considered as subsurface doping of semiconductor that narrows the barrier at the MS interface to the tunnel-transparent thickness. It is necessary to note that in our approach there is no other source of nitrogen except the semiconductor because annealing is performed in vacuum. This leads to more intensive nitrogen release out of the semiconductor and presumably higher concentration of vacancies than in the normal case and thus lower resistance.

The second process is a redistribution of aluminum in metal layer until the profile approaching the U-shaped form is obtained. The boundaries of new aluminum layer similar to the boundaries of titanium (titanium nitride) layer. This indicates almost uniform distribution of the aluminum particles in the contact layer. Most likely, the aluminum particles assist charge carriers in overcoming the contact layer, possibly by a process similar to the hopping conduction. Therefore, the use of titanium single layer in the structure does not allow for obtaining low contact resistance even at prolonged annealing time. In this case nitrogen is released, nitride with a transparent barrier at the boundary is formed, but its resistance is high. Aluminum reduces the resistance. It is possible that the presence of aluminum additionally reduces the height of the barrier at the boundary, may be due to formation of  $\text{TiAl}_3$  composition. The ohmic contact with low resistance is formed when titanium is not actively interacting with the nitrogen.

Both considerable time and high temperature are required for above-mentioned redistribution of atoms and formation of nitride-based and intermetallic compositions. This determines the optimal annealing time of 10 min and temperature of 750°C. Since this achieves the required uniformity of the distribution of atoms in the contact, a further increase of these parameters does not lead to the resistance improvement. Moreover, there may be some degradation of the contacts because of their partial evaporation and contamination. The optimal thickness of the layers is determined by the concentration of atoms required to form these compositions and for correct distribution of aluminum in the contact layer.

#### 4. Conclusion

We have studied the processes of atom redistribution that occur during the formation of metal compositions on the surface of epitaxial layers of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  solid solutions of n-type conductivity taking into account the influence of high-temperature treatment. The ohmic behavior of I-V characteristics can be achieved by annealing in vacuum for 10 min and at a temperature no less than 750°C for double-layer Ti/Al compositions. Investigations by AES revealed that annealing leads to the release of nitrogen from the epitaxial layer and the formation of titanium nitride composition in the surface layer accompanied by the appearance of nitrogen vacancies. Lack of nitrogen in the annealing chamber may contribute to this process. In addition, the redistribution of aluminum in the surface layer with a possible formation of intermetallic composition is observed. These processes contribute to a significant reduction of the contact resistance.

Based on conducted research the technology for creation of Ti/Al/n- $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ohmic contacts by vacuum thermal evaporation approach was developed. The optimal thickness of Ti and Al layers was determined (15 nm and 35 nm, respectively) as well as time parameters and temperature parameters of

annealing. The main feature of the technology is the creation of ohmic contacts with subsequent annealing in vacuum instead of nitrogen or argon. Achieved contact resistance is equal to  $8 \cdot 10^{-5} \text{ ohm} \cdot \text{cm}^2$ .

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