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Low-temperature treatment of Al/Ti nanolayers to form solid solution in order to improve the ohmic contacts process formation

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Abstract. Heat treatment of the Al, Al/Ti and Au/Ni/Al/Ti nanolayers at 450 °C was studied by measuring transparency, resistivity and also by SIMS (secondary ion mass spectrometry) and XPS (X-ray photoelectron spectroscopy). Heat treatment has led to the increase in transparency and in resistivity of Al/Ti films. On the contrary, the same treatment for the pure Al layer decreases resistivity but transparency increases due to the decrease in the unoxidized Al thickness. The upper Au/Ni layer has led to greater changes in resistivity and transparency but presumably due to a higher oxidation degree, that confirmed by XPS. Observed changes of the Al/Ti layer structure are assumed to be explained not only by oxidation, but also by the partial formation of a Ti-Al solid solution, confirmed by SIMS (Ti and Al redistribution in the layer). The suppression of oxidation, Ti-Al formation temperature reduction and, as a result, possibility to improve GaN HEMT ohmic contacts with such layers were studied.

Keywords: thin film, rapid thermal annealing, ohmic contact, TiAl compounds, transparency, Raman spectroscopy, SIMS, XPS

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Низкотемпературная обработка нанослоев Al/Ti для формирования твердого раствора с целью улучшения процесса создания омических контактов

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Аннотация. Исследована термообработка при 450 °C нанослоев Al, Al/Ti и Au/Ni/Al/Ti с анализом их прозрачности, удельного сопротивления, а также с применением ВИМС (вторично-ионная масс спектрометрия) и РФЭС (рентгеновская фотоэлектронная спектроскопия). Термообработка привела к увеличению прозрачности и сопротивления пленок Al/Ti. Аналогичная обработка чистого Al, напротив, снизила сопротивление, но увеличила прозрачность за счет частичного окисления. Верхний слой Au/Ni обусловливает более сильные изменения прозрачности и сопротивления, вероятно, из-за большей степени окисления, подтвержденной РФЭС. Однако общие изменения прозрачности и проводимости структуры слоев Al/Ti могут быть объяснены частично окислением, и частичным формированием твердого раствора Ti-Al, подтвержденным перераспределением Ti и Al по ВИМС. Таким образом, предложена возможность снижения температуры формирования, окисления и улучшения омических контактов к GaN HEMT для таких слоев.

Ключевые слова: тонкая пленка, быстрый термический отжиг, омический контакт, соединения TiAl, прозрачность, комбинационное рассеяние света, ВИМС, РФЭС

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Introduction

The temperature of ohmic contacts formation of GaN HEMT during rapid thermal annealing (RTA) is caused by the necessity of the Ti atoms redistribution, that is crucial in the reactions between N and Ti, Al, with formed at the same time Ti-Al compounds solid solutions [1]. However, high temperature of RTA negatively affects the electrical parameters of the heterostructure, and reducing the RTA temperature is an important issue [2]. The temperatures > 800 °C are being used to form ohmic contacts in the traditional methods, e.g. RTA [1] or laser annealing, can affect the characteristics of the structure due to degradation of the GaN layer and oxidation of Ga and Al [3, 4]. It is proposed to use the nanolayers (< 3 nm), which melting point is lower [5], than the bulk material's one [6], to reduce the RTA temperature. Thus, it is possible to form an Al-Ti solid solution and activate processes, necessary for the ohmic contact formation at the lower temperatures. Low resistance contacts are formed at 500 °C [2]. This confirms that TiAl and TiN are formed at temperatures much lower than the Al-Ti melting points shown in the phase diagram [6]. The mechanism of this decrease in temperature remains unclear. The phase diagram shows that the formation of the Ti-Al alloy is both the cause and the necessary condition for the formation of ohmic contacts at temperatures below the melting point of pure Ti. RTA can cause the damage of AlGaN surface, which is one of the main reasons of GaN HEMT degradation and poor performance [3]. XPS analysis has shown that the damage to the AlGaN surface is associated with an oxidation reaction under high temperature. In this work, the problem of Ti-Al formation using nanolayers was investigated with low temperature process, slightly below the lowest temperature of ohmic contact formation for such layers [2], which was 450 °C. Such low temperature will avoid damage to the AlGaN surface and maintains the electrical characteristics stability of GaN HEMT, as well as reduces stress formation in the GaN on Si substrate during RTA.

Materials and Methods

Two structures deposited by electron-beam evaporation (0.25 Å/s) on Si substrates with 300 nm SiO_2 were studied: Al (11.2 nm)/Ti (2.3 nm)/Al (11.2 nm)/Ti (2.3 nm); and similar structure with

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additional layers of Au (3 nm) and Ni (3 nm) on top Au (3 nm)/Ni (3 nm)/Al (9 nm)/Ti (2 nm)/Al (9 nm)/Ti (2 nm). Single layer of Al (~30 nm) was used as the reference structure. Thermal treatment was performed in a chamber in the Ar atmosphere with a flow rate of ~1 l/min at the annealing to 450 °C, rate of 20 °C/min. The resistivity of the metal layers was measured using the 4-probe method. The resulting transparency of the layers before and after heat treatment was investigated using Raman by comparing the signal (Centaur U HR, Nano Scan Technology) from Si with and without metal layers on top. Atomic force microscopy (AFM, Solver-Pro, NT-MDT) was used to monitor the thickness (to estimate oxide growth) and roughness of metal films. In addition, the elemental composition was analyzed using secondary ion mass spectrometry (SIMS, ToF.SIMS 5-100, Ion ToF) on the same samples of Au/Ni/Al/Ti/Al/Ti before and after annealing at 450 °C. An O_2^+ ion beam with an energy of 500 eV for sputtering and an analytical Bi^+ beam with an energy of 30 keV were used. When processing the SIMS data, the $^{58}Ni^+$, $^{54}Al_2^+$, and $^{49}Ti^+$. signals were normalized to the maximum current of each ion and then normalized to the total signal. An X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD, Research Facility Center at the Institute of Solid State Physics RAS) study with Ar^+ 5 keV ion etching was also performed for the same samples before and after annealing at 450 °C. XPS analysis shows the percentages of Ni, Al, Ti, Si, Au and O, also the contribution of SiO_2 has been subtracted that shown separately.

Results and Discussion

The total thickness of the Al/Ti sample after annealing increased from 29.5 nm to 31.8 nm: the thickness of the unoxidized Al layer decreased by 1.1 nm due to the partial oxidation (Fig. 1, *a*). Annealing of Al/Ti at 450 °C led to the increase in the film transparency from 14.1 to 23.5% (1.7 times, Fig. 2, *a*, *b*), as well as its resistivity – from 64 μΩ·cm (similar to the reference Al sample at 25 °C) up to 128 μΩ·cm (2 times) (Fig. 2, *c*). Similar measurements were performed for Al without a Ti layer. Due to the decrease in the thickness of unoxidized Al by 3.3 nm caused by partial oxidation (total layer thickness increased from 36.4 to 42.9 nm), the transparency increased from 18.9 to 23.2% (1.2 times), while the resistivity decreased from 75 μΩ·cm to ~27 μΩ·cm due to integration from initially formed clusters. Observed transparency changes align with the dependence of transparency on the thickness of unoxidized Al [7]. Significant Al sample thickness changes in the absence of Ti also indicates a difference in the oxidation mechanism of the upper Al layer (~11 nm) and an influence of the Ti sublayer. At the same time, the single Ti layer itself (~2.5 nm) is completely oxidized after 3 days in air without heating. The resulting TiO_2 (~4.5 nm) layer shows negligible presumably anti-reflective coating effect [8] as a slight increase of the Si Raman peak intensity (Fig. 2, *a*). Therefore, a higher oxidation depth increase was expected rather for Al/Ti than Al.

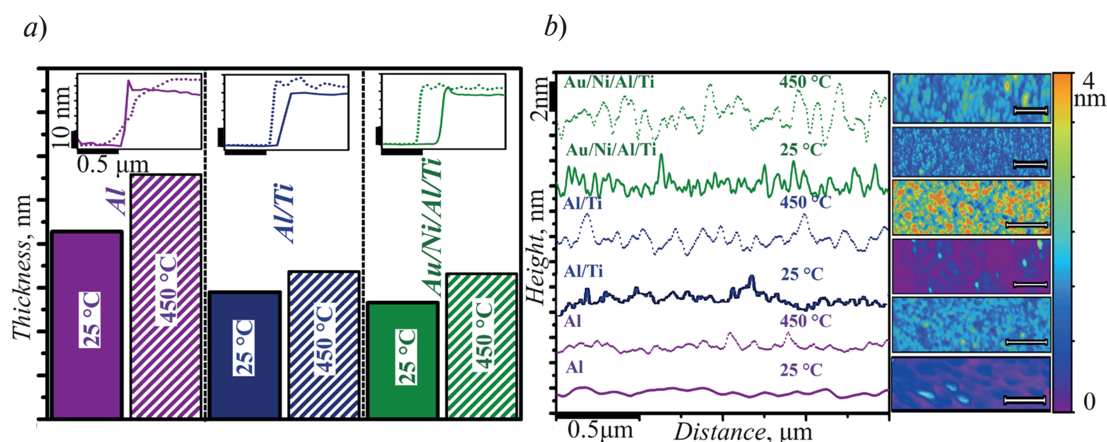

Fig. 1. AFM data of the layer thickness at the edge (*a*), AFM surface morphology and cross sections (*b*)

The roughness increase of Al/Ti compared to Al was observed (Fig. 1, *b*, all scale bars are 0.5 μm), which also indicates a difference in the layer's structure during annealing. The layers remained continuous even after annealing, so changes in the layer resistance cannot be explained by its

clustering. From the opposite changes in the resistivity of Al/Ti and Al, with co-directed changes in transparency with a greater change for Al/Ti, it can be assumed, that the Al Ti solid solution is partially formed, since the resistivity exceeds the reference sample of pure Al at 25 °C only in 2.2 times [9]). However, Ti-Al solid solutions can presumably form only at higher temperatures (480–520 °C), since the formation of ohmic contacts for such layers has been demonstrated [2], at which changes in the Ti layer are inevitable. However, noticeable changes in Al/Ti appear already at 450 °C. In the samples with Au/Ni top layers, there was a small difference in thickness (from 28.3 to 31.6 nm), indicating a small oxidation effect with annealing, but greater than one for the Al/Ti structure without a top layer (Fig. 1, *a*). For a sample with Au/Ni, transparency and resistance changed from 11.4 to 31.5% and from 27 to 183 μΩ·cm (Fig. 2). These changes are higher than for the Al/Ti and can be explained by the Au-Al, Ni-Al alloys formation (resistivity increase despite similar oxide fraction).

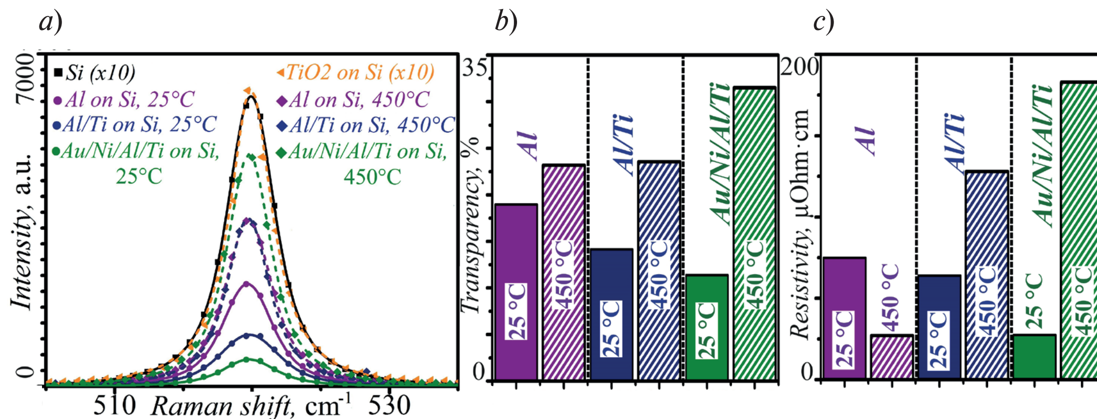

Fig. 2. Suppressing of the Raman of Si by metal (*a*) and estimated transmittance (*b*), resistivity (*c*)

Partial oxidation at a significant depth of the Ni-Al alloy was observed, due to it can be formed at the lower temperatures than Al-Ti [10]. Thus, the presence of Ni and Au in the depth demonstrates its low effectiveness as a protective layer, aligned with other results [1]. It is shown by SIMS that 1/4 of the depth of the structure is Ni/Al or Au/Al composite or alloy (Fig. 3, *a*). The Ni-Al alloy oxidizes at a significantly higher rate than Al-Ti [11, 12]. This explains the greater depth of oxidation and thickness changes. However, deep in the layer, where the contribution of Ni is negligible, SIMS has shown significant Ti redistribution, which directly confirms that at 450 °C layers start to change, which is important for the ohmic contacts formation. In contrast, for the sample at 25 °C the individual layers of Ti can be resolved (Fig.3, *a*). Presumably a Ti-Al compound with an elemental ratio similar to $TiAl_2$ or $TiAl_3$ was formed in areas where mainly Al was present before annealing, which is caused by the use of nanolayers (with clusters < 3 nm).

The presence of Ni in the deep layer of Ti even before the thermal treatment was caused by the non-uniformity of the etching rate in the studied area of 300×300 μm (with increased surface roughness). The sample without heat treatment contained up to ~10% Ni at the 1/4–1/3 of its depth (Fig. 3, *a*). The resistance of Al-Ti can differ from Al by 10 times [9]. However, even considering the contribution of Ni-Al or Au-Al, the resistance has increased only in 6 times, which indicates the partial formation of Al-Ti alloys in combination with the partial redistribution of Ti at 450 °C (this is not enough to achieve the minimum resistance of ohmic contacts, that obtained only at 500 °C [2]). The resistance of the Au-Al alloy is less than ~15 μΩ·cm [13], which is significantly less than the resistance of Al/Ti (about 50 μΩ·cm [9]). Thus, the formation of the Au-Al alloy is most likely a limiting factor for the growth of the resistance of the whole structure, as well as for the Ni-Al alloy [14]. Thus, these alloys' contribution to the increase in resistance is insignificant, considering their content and thickness (not more than 1/3). The increase in transparency and resistivity can be partially explained by the fact that the oxidation rate of $NiAl_3$ is an order of magnitude higher than that of $TiAl_3$, meaning that thin layers of Au/Ni are more likely to increase the contribution of oxidation compared to Al/Ti. The observed difference in transparency and resistivity for

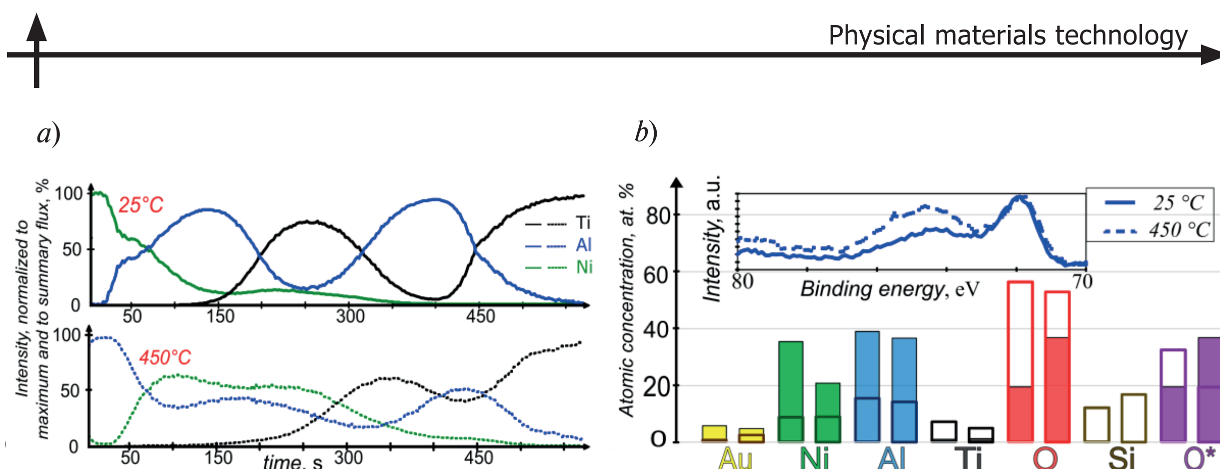

Fig. 3. Au/Ni/Al/Ti sample before and after annealing: SIMS profiles (*a*), XPS: left – 25 °C, right – 450 °C. Empty columns – elements in the depth of the layer (Ar^+ 500 s etching), and filled – in first ~1/4 in depth (100 s etching); * – oxygen not associated with Si; inset: Al 2p peak of 100 s etch (*b*)

Au/Ni/Al/Ti greatly differs from Al/Ti. The redistribution of Ni and Au can probably contribute to the redistribution of Ti and Al with the formation of Ti-Al over most of the layer thickness. Without an analysis of the oxides' contribution in layers it is impossible, even according to SIMS data, to entirely confirm the formation of the Al-Ti alloy. In the case of Ti/Al, the small thickness (up to 4 nm) of the oxide layer on Al limits further oxidation, in contrast to the possibility of deeper oxidation in Ni-Al layers. Thus, it is important to evaluate the oxides' contribution for Au/Ni/Al/Ti sample, which was performed by XPS. The sample after 450 °C shows a redistribution of Au and Ti in depth, but it similar to the one at 25 °C (Fig. 3, *b*). The presence of Ni, Ti, Al on XPS both after 100 s and 500 s of etching, combined with the presence of Si after 500 s, indicates that the initial homogeneity and structure of the layers' thickness have changed even for the sample without heat treatment. It indicates modification of the layer by Ar^+ ion beam during etching in XPS. In contrast, the redistribution and the formation of alloys in the depth of the layer, which is inhibited due to the parallel oxidation process [15], during sputtering with an O_2^+ ion beam in SIMS (with an energy of 500 eV), shows individual Ti layers at 25 °C (Fig. 3, *a*). An analytical Bi^+ beam etches in smaller area (30 µm diameter in contrast with 400 µm for XPS) during pulsed sputtering in SIMS, therefore there is less contribution of inhomogeneities in depth on that area, and the differences between 25 °C and 450 °C samples are significantly larger in contrast to the XPS data. The sample at 25 °C in the depth (at 500 s, when Si from the substrate appears) shows a high proportion of metal oxides, unbound with SiO_2 (~70 %), which can be explained by the oxidation of metals during sputtering of SiO_2 with an Ar^+. The sample after 450 °C has only ~45% share of metal oxides at both smaller and greater depths. It can be explained by the formation of $TiAl_3$, which has greater resistance to oxidation compared to NiAl [11, 12]. However, at the lesser depths (100 s, no Si signal) the proportion of oxides is ~20% for the 25 °C sample and ~45% for the sample after 450 °C (Fig. 3, *b*, in inset higher intensity above 73 eV with adjusted to intensity ca. 72 eV), which indicates that additional partial oxidation occurs during heat treatment. The equivalent thickness of a continuous unoxidized Al for a sample at 25 °C in terms of optical transparency is not ~16 nm (according to a quartz sensor during deposition), but 13 nm [7], corresponding to the measured transparency of ~11 % (Fig. 2, *b*), with 20% oxidation. However, the transparency of a 45% oxidized layer should be equivalent to a 8 nm layer, which corresponds to ca. 22% transparency. The Au/Ni/Al/Ti structure after 450 °C, has a transparency of 32% (Fig. 2, *b*), which is higher than the value estimated with a fraction of oxide from XPS data. This indicates that the observed transparency increase cannot be entirely explained only by the oxidation with residual oxygen processes during the heat treatment. The formation of Ni-Al, Au-Al compounds at the temperature lower than the Ti-Al one may precede and stimulate the formation of Ti-Al due to the redistribution of the materials. However, Au and Ni layers also lead to an oxidation contribution increase, caused by Ni-Al compounds formed at the temperatures lower, than the ones with Ti-Al.

Conclusion

Analysis of changes in thickness, resistivity, transparency, and elemental distribution, along with changes in the oxide proportion after 450 °C heat treatment according to SIMS and XPS data, indicates that nano-sized Al/Ti layers with 2–3 nm Ti can provide the $TiAl_3$ solid solution formation partially and also Ti redistribution. The addition of upper Au/Ni layers to the Al/Ti structure does not suppress the oxidation during heat treatment, but on the contrary, it can increase the oxide proportion, due to the formation of Al-Ni compounds, at the depths greater than the oxidation of the continuous Al layer. That explains the possibility of increasing the oxide proportion in Au/Ni/Al/Ti compared to the Al/Ti during heat treatment. However, changes in transparency and conductivity cannot be fully explained by oxidation, but can only be explained by the possibility of partial Ti-Al compound formation with the higher resistivity compared to Al. Similar processes of Ti redistribution and the Ti-Al alloys formation are important and necessary for the ohmic contacts formation using RTA in GaN HEMT structures. The features demonstrate the possibility to reduce the formation temperature, the oxidation processes and, as a result, the possibility to improve the ohmic contacts based on such layers.

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