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Interfacial Reactions and Electrical Properties of Ti/n-GaN Contacts

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Abstract

The phase equilibria in the ternary Ti-Ga-N have been investigated. Interfacial reactions in Ti/GaN contacts have been studied by diffusion couple experiments. The ternary phase Ti_2GaN was confirmed by x-ray diffraction in bulk samples as well as in massive Ti/GaN diffusion couples and annealed Ti thin films on GaN. The diffusion path in samples, annealed at 850°C in Ar gas, is GaN/TiN/Ti_2GaN/Ti_3Ga/Ti. A planar TiN layer forms in direct contact to GaN and governs the electrical properties of annealed Ti/GaN contacts. Thin film contacts were fabricated by sputtering Ti on MOVPE grown n-GaN ($5x10^{17}cm^{-3}$) and subsequent rapid thermal annealing in an Argon atmosphere. Initially non-linear current-voltage characteristics become ohmic after annealing and a specific contact resistance of approximately $10^{-2}\ \Omega cm^2$, measured with the circular transmission line method, was found after annealing at 900^0C for 1 min.

1. Introduction

With the recent success in the development of gallium nitride based devices, such as blue LEDs and laser diodes, the fabrication of reliable ohmic and Schottky contacts to GaN has become a more important issue. Making reliable ohmic contacts to wide band gap semiconductors with sufficiently low contact resistance is usually a difficult task. Although a Schottky barrier height of 0.58 eV was measured for Ti on n-GaN [1], several ohmic contact structures with Ti have been used [2] [3] [4]. The contact with the currently lowest observed specific contact resistance ($8x10^{-6}\ \Omega\ cm^2$) on n-GaN is fabricated by deposition of a Ti/Al bi-layer followed by an Rapid Temperature Annealing (RTA) at 900°C for 30 sec [2]. The specific contact resistance could be improved even further by the use of pre-deposition reactive ion etching (RIE) and the introduction of an additional Ni/Au capping layer leading to a rather complex contact structure [5]. Both contacts are not understood in detail yet and explanations are speculative. As Lin at al. [2] pointed out, an analysis of the interface zone of the contact is hampered by the absence of the quaternary Ga-N-Ti-Al phase diagram. In a recent survey of transition metal-Ga-N phase equilibria a tieline between TiN and GaN was predicted in the ternary Ti-Ga-N by approximate calculations; however, a ternary phase was not included due to the lack of thermodynamic data [6]. These data as well as the knowledge of the interface morphology between contact and semiconductor are essential for the development of a reliable, thermally stable contact technology.

The purpose of this study is:

- to provide the present fundamental data about the phase equilibria in the ternary Ti-Ga-N phase diagram
- to study the Ti/GaN interface by means of diffusion couple experiments
- to fabricate and characterize electrical Ti/GaN contacts and correlate their properties with the observed interface behavior.

These data can possibly lead to a better understanding of the currently used contact structures and provide a starting point for the investigation of the more complicated phase relations in the quaternary Ti-Al-Ga-N system.

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2. Phase equilibria in the Ga-N-Ti system

2.1. Approximate Calculation and Review of the Literature

In the binary Ti-Ga system up to eight different phases were reported but some of the observed structures were not established as equilibrium phases [7]. In particular the region with more than 35 at.% Ga, remains uncertain. The only phase diagram in the whole composition range, given by Pötschke [8] is partly questionable due to oxide contamination of the samples. All intermediate phases, given by Murray [7] were accepted for the approximate calculation, although the existence of some phases remains uncertain.

In the Ti-N binary two phases TiN and Ti_2N exist and in the Ga-N binary only GaN. Very few data were available for the Ga-N-Ti ternary system. A ternary phase Ti_2GaN was reported [9]; however, no confirmation and no thermodynamic data were available for this phase.

An approximate calculation of the phase equilibria in the Ga-N-Ti ternary system was performed by means of the TerQuat program [10]. In this program all phases are assumed to be line compounds. The Gibbs energy for all phases was either taken from the literature, or approximated by the enthalpy of formation, as predicted by the Miedema model [11]. In the Ti-N binary Gibbs energies of -154.6 kJ/g-atom (TiN), respectively -104 kJ/g-atom (Ti_2N), were taken from Kubaschewski's compilation [12] and for GaN, a value of -70.7 kJ/g-atom [12] was used in the calculation.

The Gibbs energies for the accepted phases in the Ti-Ga binary are $TiGa_3$ (-31kJ/g-atom), $TiGa_2$ (-41 kJ/g-atom), Ti_3Ga_5 (-45 kJ/g-atom), Ti_2Ga_3 (-47 kJ/g-atom), TiGa (-51kJ/g-atom), Ti_5Ga_4 (-48 kJ/g-atom),Ti_5Ga_3 (-46 kJ/g-atom) Ti_2Ga (-44 kJ/g-atom) and Ti_3Ga (-35 kJ/g-atom).

Using the above data for the calculation, a minimum Gibbs energy of formation of -103 kJ/g-atom is required for Ti_2GaN to be stable at room temperature. The isothermal section of Figure 1 was calculated using a value of -110 kJ/g-atom.

According to the approximate calculation the connection line between GaN and Ti is crossed by several tielines, hence an interface reaction in Ti/GaN diffusion couples is almost certain. It can also be seen that a three phase field GaN-Ga-TiN forms, which leaves TiN or Ga as possible phases in contact to GaN. However, if the estimated Gibbs energy for Ti_2GaN is lowered below -115 kJ/g-atom, a GaN-Ti_2GaN tieline would form, the most likely reaction mechanism in diffusion couples would be altered and Ti_2GaN would be in direct contact with GaN.

This means that the existing thermodynamic data in the system are not sufficient to predict the phase equilibria without doubt; however, few selected samples in the ternary system or the experimental observation of a diffusion path are sufficient to verify the approximate calculation of phase equilibria and in turn give a range for the Gibbs energy value of the ternary compound.

2.2. Experimental phase diagram study

The experiments were focused on the verification of the ternary Ti_2GaN phase, since no report other than from Jeitschko [9] was available. Starting materials were TiN, Ga and Ti with 3N purities. The nominal composition was weighted, thoroughly mixed and cold pressed to a pellet. The sample was then sealed in an evacuated silica tube and annealed at 850°C for 160 hours. After quenching in water the sample was studied by XRD with CuKα radiation.

The quenched sample was visibly two-phase. Most of it consisted of a dark gray phase, which was separated from the gold colored TiN with tweezers. The dark phase was powdered and resulted in an almost single phase XRD-spectrum (Figure 2) which was almost identical with the calculated spectrum from literature data [13] (using [14]). Only a small peak could be attributed to the strongest TiN refraction. This result confirms that Ti_2GaN is a stable phase at 850°C; however, additional experiments or the identification of a diffusion path are necessary to obtain the tielines in the system.

3. Diffusion studies

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3.1. Experimental

In order to investigate the reaction zone between Ti and GaN several Ti/GaN diffusion couples were prepared. Starting materials for massive diffusion couples were thick layers of GaN (80 μm), grown by Halide Vapor Phase Epitaxy (HVPE) on (0001) sapphire [15] and a Ti foil which was cleaned in HF:H_2O (1:1) solution before use. Both, Ti foil and GaN substrate, were placed above each other and were cold pressed with Ti powder to a pellet of 5 mm diameter. The samples were sealed in silica under several mbar argon atmosphere and annealed at temperatures between 700°C and 850°C. After quenching, the pellets were embedded in epoxy and a cross section through the reaction zone was prepared metallographically by grinding and polishing. The polished sections were examined by optical microscopy as well as by scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDX). From a linescan across the interface the diffusion path could not be identified unambiguously because a quantitative determination of the N content was not feasible.

For this reason a second preparation method for diffusion couples was applied to determine the phase structure in the interface zone by XRD and to verify the suspected Ti_2GaN phase in the sample. A thick Ti layer (≈400nm) was sputter deposited onto the GaN substrate and the sample was subsequently annealed in a sealed silica tube at 850°C for 24 hours to ensure a complete reaction of the film.

An XRD-spectrum of the thin film was measured in glancing angle X-ray diffraction mode with a 10° angle of incidence.

3.2. Results

A cross sectional view of the reaction zone of a sample annealed at 850°C for 2 days is shown in Figure 3a. The corresponding EDX line scan in Figure 3b gives a qualitative measure of the Ga and Ti content across the interface. A basically planar layered structure can be observed with a thin dark layer in direct contact to GaN. From the little drop in Ga content at the interface and from the darker color in the Back Scattered Electron image, which corresponds to lower density of the phase, it is clear that a thin TiN layer forms at the interface. A more significant drop in Ga content was not observed because the excitation volume of the electron beam and the TiN layer thickness have comparable size. The subsequent, much thicker, layer is most likely Ti_2GaN followed by a Ti_3Ga layer close to the Ti. Within the Ti_3Ga layer voids developed in all samples.

The Ti_2GaN phase was also verified by XRD in the completely reacted thin film sample, as shown in Figure 4. In addition, a strong GaN peak and the strongest peaks of the Ti_3Ga and TiN phases were identified in this sample. However, not all peaks could be attributed to possible reaction products. They probably correspond to phases caused by oxygen contamination.

4. Electrical characterization of Ti/GaN contacts

4.1. Experimental

Epitaxially grown n-GaN layers of approximately 2 μm thickness on (0001) sapphire with AlN bufferlayers were used as substrate material. The growth was carried out in a horizontal MOVPE reactor with Trimethylgallium, Trimethylaluminium and ammonia as reactants. A X-ray double crystal scan of the 002 GaN peak revealed a full width half maximum of 380 arcsec. Unintentionally doped layers had typically a carrier density of 2-5x10^{17} cm^{-3} and a Hall mobility around 300 cm^2/V sec Before deposition of the contacts the surface was cleaned by degreasing in ultrasonically agitated trichloroethylene, acetone and methanol for 5 minutes each. In a second step the GaN was etched in boiling NaOH solution for 5 min and subsequently rinsed in deionized (DI) water.

Photo lithography with lift-off was applied to fabricate the contact pattern. Before metal deposition the contact holes were etched again using various solutions, that were reported in the literature. For the contact measurements, presented in this paper, a HCl:H_2O (1:1) solution was used for 5 min, followed by a DI-H_2O rinse. Afterwards the substrates were blown dry with nitrogen and immediately transferred to a sputter chamber with a base pressure of 5x10^{-7} mbar.

Polycrystalline Ti-contacts were sputter-deposited with a typical thickness of 100 nm at a sputter rate of approximately 0.1 nm/sec and with an accelerating voltage of 290 V. Several ring patterns of different size were

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deposited on the substrate for circular transmission line measurements [16]. The inner contact dot had a radius between 30 and 50 μm.

Besides these structures to measure the specific contact resistance of the annealed contacts, part of the substrate was prepared as a large area Al contact in order to measure the barrier height of the as-deposited Ti contacts. Al forms an ohmic contact even in the as-deposited state, but degrades rapidly upon annealing [2]. One half of the patterned substrate was covered by a metal foil and an Al layer was sputter deposited on top of some Ti structures, in order to form a large ohmic contact area. After annealing at higher temperature the current flow occurs mainly across the Al/Ti structures. The current-voltage (I-V) characteristics were measured between the inner contact dots and the large ohmic contact area. Electrical characterization was performed using a Source Measure Unit (Keithley 236) and copper beryllium needle probes. Various annealing procedures between 400°C and 900°C for 60 sec were used in a AG Associates Mini Pulse RTA-furnace under a purified Argon atmosphere. The heating rate for all experiments was 30°/sec.

4.2. Results

Current-voltage (I-V) curves of a Ti/GaN contact, annealed at different temperatures, are shown in Figure 5. In the as-deposited state the contacts were always nonlinear. The determination of the barrier height using the I-V curve was unreliable, since the measured ideality factor had typically a value of n=3. The corresponding barrier height was ϕ_B=0.9 eV, calculated from the saturation current density with the theoretical value for the effective Richardson constant of 24 A $cm^{-2}K^{-2}$ [17].

Upon annealing at 400°C the contacts became ohmic and the I-V curves remained almost unchanged up to a 900°C, some of the corresponding I-V curves in Figure 5 are omitted for clarity. The large area Al contact showed considerable degradation upon annealing, however the reacted Ti/Al structure ensured the current flow through the ohmic contact.

After annealing at 950°C the I-V curve showed considerable degradation, but remained linear although the determination of the specific contact resistance was no longer possible with the Circular Transmission Line method due to an increased sheet resistance of the contact. The specific contact resistance for annealed contacts was in the range between 10^{-1} and 10^{-2} Ωcm^2, as shown in Figure 6 .

Various pre-deposition substrate treatments were tried in order to improve contact performance but no other wet etch solution, that was used, showed a significant improvement. However, it was noticed that lower specific contact resistance measurements were generally obtained on substrates that had experienced some heat treatment prior to contact deposition.

5. Discussion

From the combination of both diffusion couple experiments a GaN/TiN/Ti_2GaN/Ti_3Ga/Ti diffusion path could be identified at reacted Ti/GaN interfaces. The observed diffusion path is superimposed on the calculated isothermal section (Figure 1) at room temperature. With the assumption that the phase equilibria remain in principal unchanged between room temperature and 850°C, a ΔG_f value between -103 and -115 kJ/g-atom can be estimated for the Ti_2GaN phase.

The reaction mechanism in diffusion couples is not clear yet, because marker experiments were not performed, but it seems likely that the reaction front moves mainly towards the GaN layer, because the observed gaps always developed on the Ti-side of the diffusion couple.

The electrical properties can indirectly be correlated to the observed interface morphology. The measurements show that TiN forms an ohmic contact to n-GaN which is thermodynamically stable up to high annealing temperatures. From the electrical characterization a reaction between the Ti-film and the substrate seems to occur at temperatures as low as 400°C, although no reaction could be detected in massive diffusion couples that were annealed at temperatures below 700°C. However, as expected from the layered interface structure in diffusion couples, the I-V curves remain almost unchanged upon annealing at temperatures up to 900°C. This is in an indication that TiN is the only phase in contact with GaN and therefore governs the electrical properties of the alloyed contact.

The specific contact resistance of TiN contacts in this study was considerable higher than the values measured for annealed Ti/Al contacts [2] [5]. The substrates, used in this study, had a considerably lower carrier density which is

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the main cause of the observed high specific contact resistance. Guo et al. [3] had measured Ti/Ag specific contact resistance as a function of substrate carrier density and observed a rapid decrease when the carrier density becomes larger than $1x10^{18}$ cm^{-3} [3]. For similarly doped substrates their results are well in accordance with this study.

The transport mechanism in Ti-based ohmic contacts can be explained by different models. Originally a strong dependence of the barrier height on the metal work function was anticipated for GaN due to its ionic nature [18]. However, if one compares the work functions of gallium nitride (4.1 eV [19]) and polycrystalline Ti 4.33 eV [20], a much lower barrier height than our measured value or the value of Binari et al [1] would be expected. This finding can either be attributed to Fermi level pinning at the interface or to the presence of oxygen contamination at the interface, which is very likely since no Ultra High Vacuum system was used. After alloying the barrier height is determined by TiN which has a work function well below 4 eV [21]. This would explain the ohmic contact behavior by the Schottky-Mott model. Another explanation would be the formation of a Ga-enriched interface and a low barrier height determined by the low work function of Ga (4.2 eV [20]).

The second classical method for ohmic contact formation involves a highly doped surface region beneath the contact. In the present case, an increased nitrogen vacancy concentration is anticipated at the interface after reaction, leading to an increased donor concentration.

Hence, the formation of an ohmic contact by alloyed Ti-contacts might be understood as superimposed effects of a low barrier height and an increased tunneling current caused by the nitrogen depletion at the GaN/TiN interface.

Besides these classical model explanations, the substrate itself and the pre-deposition treatment of the surface seem to play important roles in contact formation. Especially the influence of different etching procedures or heat treatment of the substrate is considerable. A possible cause for different results on pre-annealed substrates might be the incorporation of hydrogen into GaN during various processing steps and its removal upon annealing at higher temperatures [22]. Another explanation is that nitrogen depletion at the interface occurs at annealing temperatures around 900° and leads to an increased donor density. This method was also used to obtain non-alloyed Ti/Al ohmic contacts by a premetallization anneal at 1120°C [23].

The discrepancies between authors who found Ti contacts to be ohmic as-deposited [3] [5] and studies who found rectifying behavior in the as-deposited state [this study] [24], can clearly be attributed to differences in substrate preparation. The former authors both used reactive ion etching which effectively removes oxide but also increases the defect density near the surface. In a recent study by transmission electron microscopy (TEM) [25] a thin TiN layer was observed even in as-deposited Ti contacts on RIE treated substrates.

All this findings support that the formation of a TiN layer is the dominant mechanism for the formation of Ti-based ohmic contacts. A thin TiN layer was identified at the GaN interface in reacted Ti/Al and Ti/Al/Ni/Au contacts [25] and thicker TiN layers seem to improve contact performance. The role of Al in these contacts, however, is still somewhat unclear. A possible explanation for the superior performance of Ti/Al contacts would be a phase other than TiN, which was not observed yet, is responsible for the contact behavior. We can speculate for example that small amounts of a ternary phase like Ti_2AlN might form at the interface. Two ternary phases are stable at lower temperatures in the Ti-Al-N ternary system [26]. The assumption of a ternary phase was also supported by RBS measurements of annealed Ti/Al contacts [27], where a mixture of all four participating elements was observed in the contact interface. For a complete view of this contact structure the more complicated phase equilibria in the quaternary Al-Ti-Ga-N system and the diffusion paths therein should be investigated.

6. Conclusion

TiN has been identified in diffusion couple experiments as a thermodynamically stable phase in contact with GaN. A layered GaN/TiN/Ti_2GaN/Ti_3Ga/Ti interface structure governs the electrical properties in alloyed Ti/GaN contacts. The electrical characterization suggests that TiN can be used as an ohmic contact material for GaN applications at high temperatures. In addition, a TiN layer could possibly serve as a diffusion barrier for additional metallizations. Since TiN is a material which is already in use in microelectronics and can be deposited by sputtering as well as by MOVPE techniques, these findings might be useful for GaN process technology.

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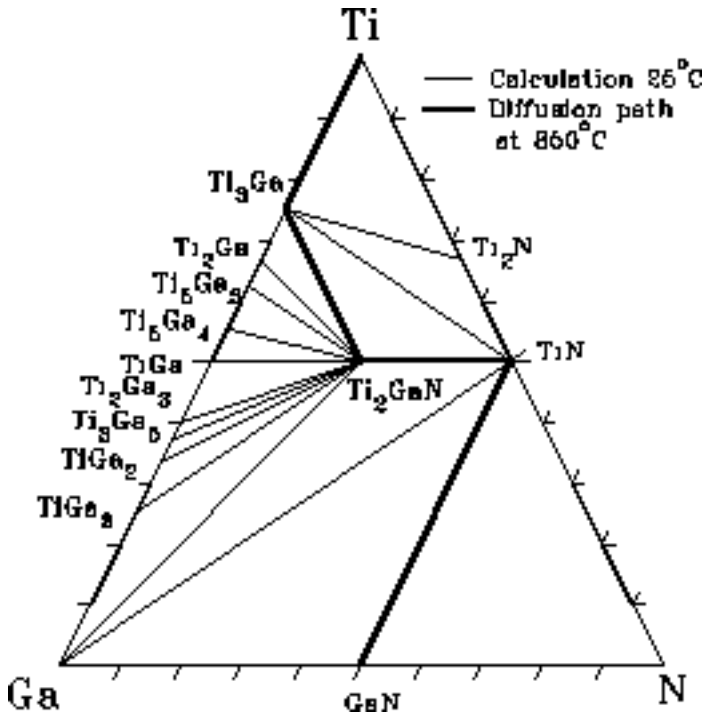

Figure 1. Isothermal section of the Ti-Ga-N system at room temperature, approximately calculated with partly estimated thermodynamic values. The observed diffusion path in diffusion couples, annealed at 850°C, is superimposed.

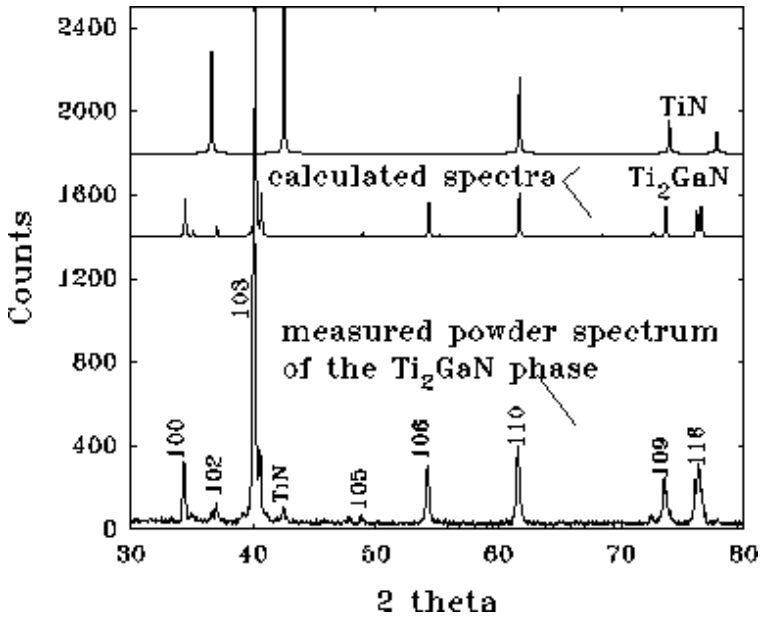

Figure 2. The ternary Ti_2GaN phase, produced by solid state reaction from TiN, Ga and Ti, was confirmed by XRD. The calculated x-ray spectra of Ti_2GaN and TiN are also given for comparison.

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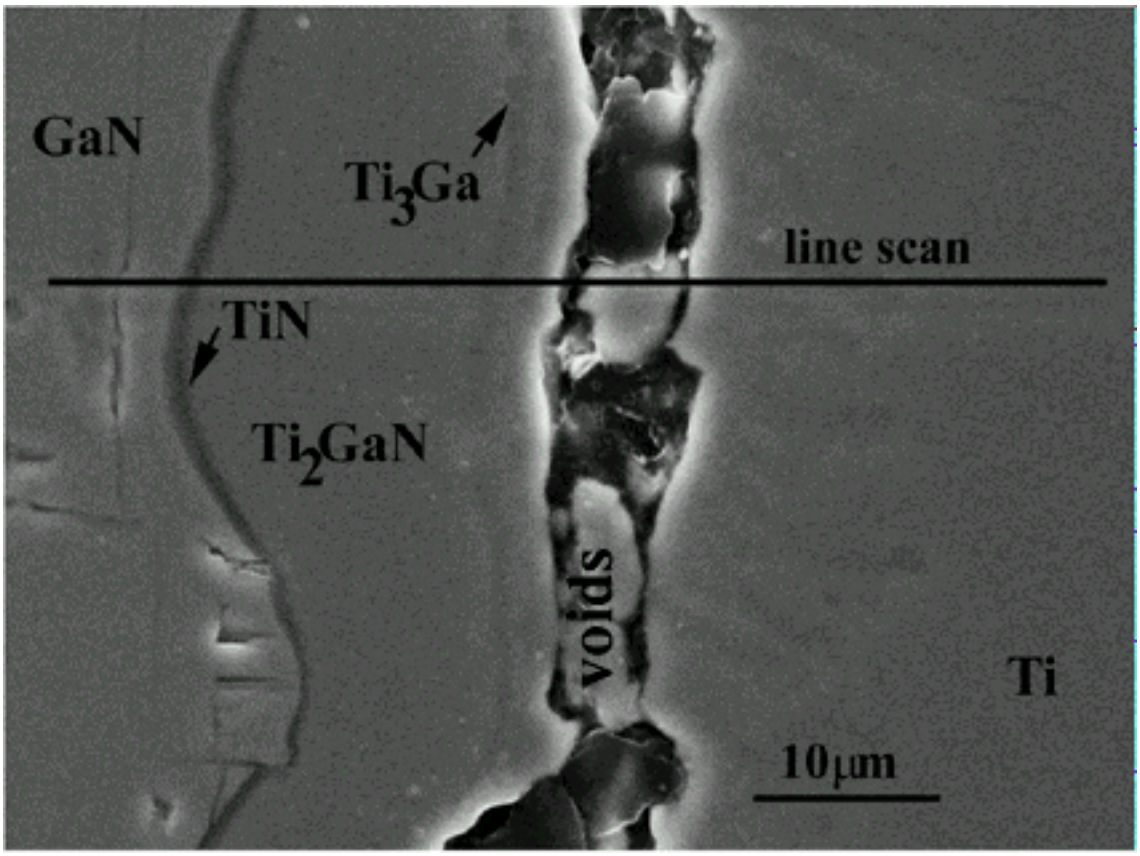

Figure 3a. Section across the interface of a massive Ti/GaN diffusion couple annealed at 850°C/2d. A GaN/TiN/Ti$_2$GaN/Ti$_3$Ga/Ti diffusion path was identified by EDX and XRD.

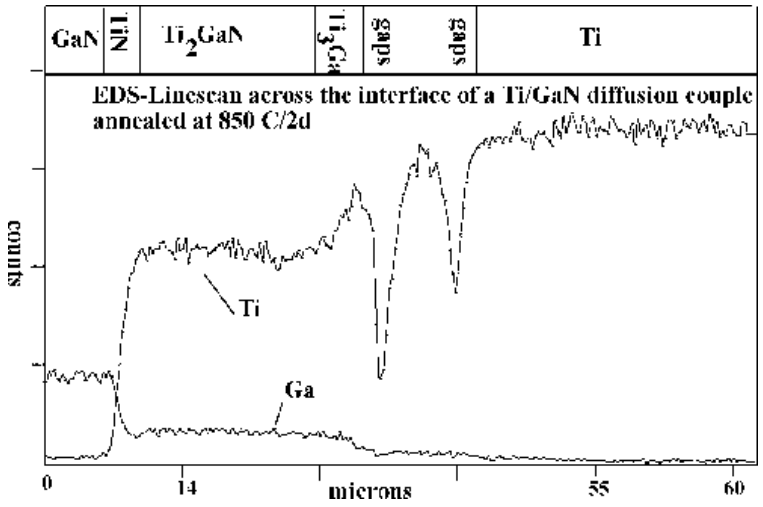

Figure 3b. Corresponding EDX line scan across the interface

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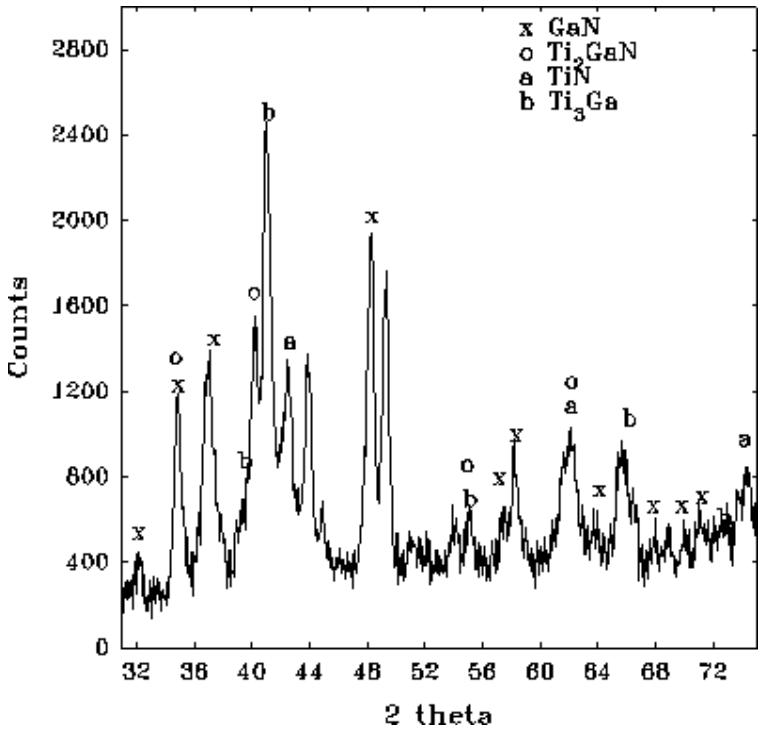

Figure 4. XRD spectrum of a thin film Ti/GaN diffusion couple, annealed at 850°C/1d, compared with spectra of reaction phases.

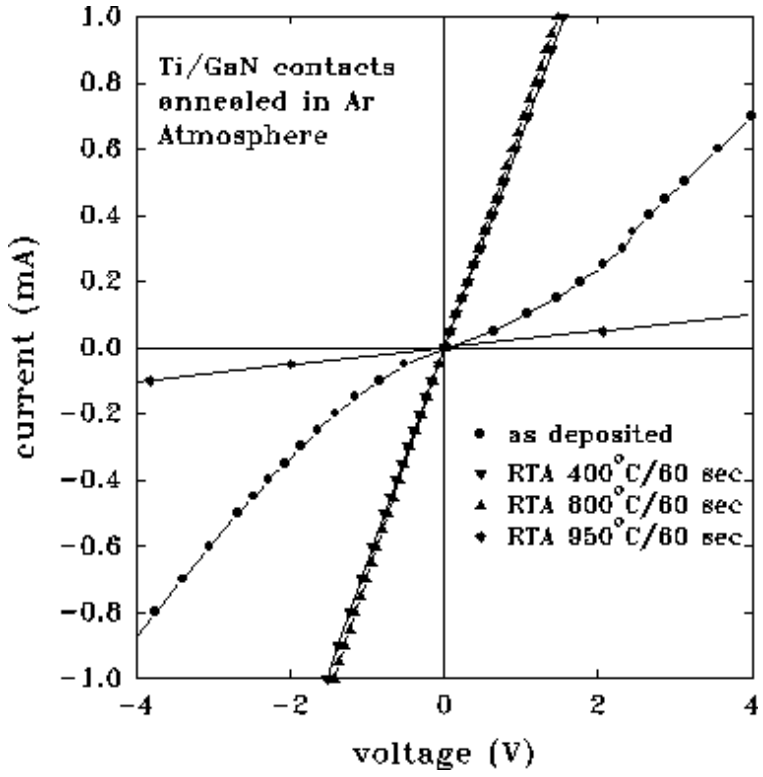

Figure 5. Current-voltage characteristics of Ti/GaN contacts annealed at various temperatures in Argon. The curves for temperatures between 400 and 800^{0}C are omitted for clarity.

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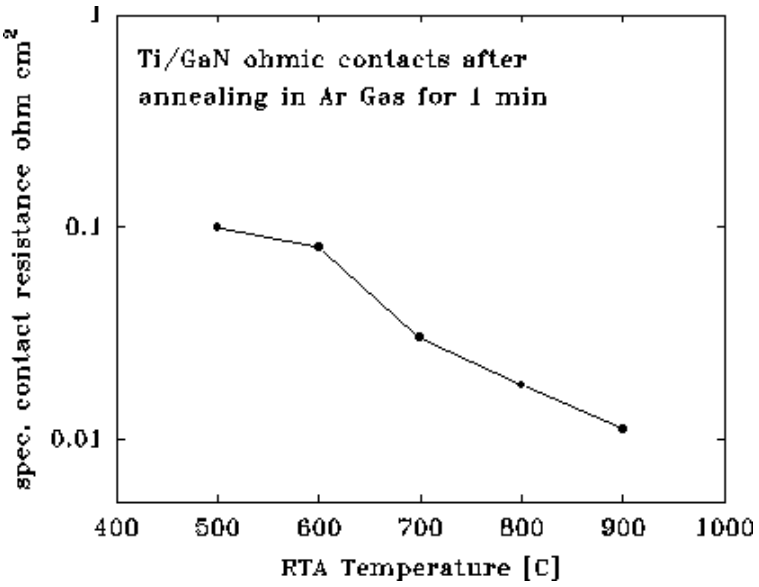

Figure 6. Specific contact resistance of Ti/GaN, measured by the circular transmission line method, as a function of RTA annealing temperature.

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