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Low Temperature (down to 450 °C) Annealed TiAl contacts on N-type Gallium Nitride characterized by Differential Scanning Calorimetry

Nicolas Thierry-Jebali^{1,2}, Olivier Menard^{2,3}, Rodica Chiriac¹, Emmanuel Collard², Christian Brylinski^{*1},
Frédéric Cayrel³ and Daniel Alquier³

¹ Laboratoire des Multimatériaux et Interfaces, UMR-CNRS 5615,

Université Claude Bernard Lyon 1, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

² STMicroelectronics, R&D department, 11 rue Pierre et Marie Curie, 37100 Tours

³ Laboratoire de Microélectronique de Puissance,

Université François Rabelais de Tours, 1 rue Pierre et Marie Curie, 37100 Tours, France.

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* Corresponding author: e-mail Christian.brylinski@univ-lyon1.fr, Phone: +00 33 4 72 43 15 16

This work reports on Differential Scanning Calorimetry (DSC) measurements performed on Ti-Al metallic layers stacks deposited on n⁺-GaN. The aim is to get better understanding of the mechanisms leading to ohmic contact formation during the annealing stage. Two exothermic peaks were found, one below 500°C and the other one around 660°C. They can be respectively attributed to Al₃Ti and Al₂Ti compounds formation. The locations of these peaks provide clear evidence of solid-solid reactions. Lowest contact resistance is well correlated with

the presence of Al₃Ti compound, corresponding to Al(200nm)/Ti(50nm) stoichiometric ratio. Subsequently, Al(200 nm)/Ti(50 nm) stacks on n⁺-GaN were annealed from 400°C to 650°C. Specific Contact Resistivity (SCR) values stay in the mid 10⁻⁵ Ω.cm² range for annealing temperatures between 450°C and 650°C. Such low-temperature annealed contacts on n⁺-GaN may open new device processing routes, simpler and cheaper, in which Ohmic and Schottky contacts are annealed together.

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1 Introduction By using wide band gap semiconductors, such as SiC, GaN and AlGaN, real performance breakthrough has been demonstrated for high power, high temperature and high frequency devices, over the previously existing devices based on group-IV and III-V lower band-gap semiconductor materials.

Fast rectifier is one of the key devices in any switching converter. 4H-SiC based Schottky diodes are now commercially available from at least 3 sources in the world.

However, bulk SiC substrates are very expensive and the hetero-epitaxial SiC layers on low cost substrates still have too many crystal defects.

These are the main reasons for the on-going research programs towards GaN-based Schottky rectifiers on both Silicon and Sapphire substrates [1].

The successful III-N LED industrial development has provided the epitaxy process for high-quality thick GaN layers grown on sapphire substrate. First characterization results on GaN-based Schottky rectifiers reported in the literature [1] seem to be comparable to those on 4H-SiC diodes, despite the high dislocation density ($> 10^9$ cm⁻²) within the GaN layers.

Ohmic contacts represent a major technological brick for device processing. On n-type AlGaIn and GaN materials, many variants of Ti-Al based contact metallization have been proposed, such as: Ti/Al [2-5], Ti/Al/Ni/Au [6], Ti/Al/W/Au [7], and Ti/Al/Mo/Au [8]. Some of them are already used for industrial manufacturing of optoelectronics and microwave devices. Generally, these con-

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tacts are annealed up to 900 °C and their “Specific Contact Resistivity” (SCR) ranges in the low $1.10^{-6} \Omega \cdot \text{cm}^2$.

On these high-temperature annealed ohmic contacts, the usual model to explain low SCR values involves: (1) the migration of N elements from GaN towards Ti to form TiN semi-metallic compound, (2) resulting nitrogen vacancies, acting as donors. However, it very likely that this model cannot apply to contacts obtained at much lower temperature, for which there is no evidence of any TiN phase formed [2,3].

For Schottky rectifiers, a good compromise has been found [5] using Al(200 nm) Ti(50 nm) on n^+ -GaN, annealed 3 minutes at 650 °C under Ar at atmospheric pressure by Rapid Thermal Annealing (RTA). This process reproducibly yields SCR values in the mid $10^{-5} \Omega \cdot \text{cm}^2$ range.

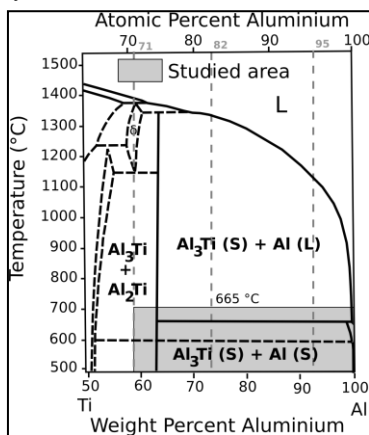


Figure 1 Al-rich extract of the Ti-Al binary phase diagram [9].

For Ti-Al-only ohmic contact on n^+ -GaN, Ti/Al ratio seems clearly the most important parameter driving the SCR value. X-ray diffraction (XRD) measurements [4] have shown that the Al_xTi phases formed during the annealing process are those predicted by the Ti-Al binary phase diagram. Best SCR results are obtained for atomic ratio Al/Ti ~ 3 , strongly suggesting that Al_3Ti (metal) / GaN (semiconductor) is indeed the Schottky configuration providing the low SCR at low annealing temperature [3, 5].

X-ray photoelectron spectroscopy (XPS) profiling [2, 3], performed on Al(200 nm)/Ti(70 nm)/ n -GaN, after 600 °C annealing, has evidenced that the Al/Ti atomic ratio keeps constant around 3 within the whole metallic phase, confirming Al_3Ti as the only detected phase in direct contact with GaN. No evidence for TiN layer has been found. It has also been identified that Al diffuses throughout the metallic layer and comes in direct contact with the GaN material.

In this work, to understand the kinetic of Al_xTi compounds formation, we have performed Differential Scanning Calorimetry characterisations.

2 Experiments

2.1 Samples Differential Scanning Calorimetry samples are described in Tab. 1. Metallic stacks were deposited

by sputtering, on both GaN epilayer and bare sapphire substrate, to discriminate Ti-Al reactions, from possible Metal-GaN reactions. Ti/Al ratios within the different metallic stacks were chosen to explore the main different configuration within the binary phase diagram and form the different Al_xTi intermetallic compounds during the DSC characterization annealing (Fig. 1).

Samples for electrical measurements were made on GaN epitaxial layer on a c-plane sapphire substrate, $3.2 \mu\text{m}$ thick and $5.8 \times 10^{18} \text{ cm}^{-3}$ Si-doped, by the following process [5]: (1) SC1+HF surface cleaning, (2) Al(200 nm) Ti deposition by sputtering, (3) photolithography, (4) Wet etch (ANPE for Al, HF 1% for Ti), and (5) annealing by RTA under Ar ambient during 3 min at atmospheric pressure. Annealing temperature range was $400 \leq T \leq 650 \text{ °C}$ with 50 °C temperature increment.

Table 1 DSC samples description.

| Metallic stacks on both GaN and Sapphire substrates | Atomic Al % |
|---|-------------|
| Al(200 nm)/substrate | 100 |
| Al(200 nm)Ti(20 nm)/substrate | 95 |
| Al(200 nm)Ti(50 nm)/substrate | 82 |
| Al(200 nm)Ti(100 nm)/substrate | 71 |

2.2 Characterization conditions DSC measurements were performed using “Metler-Toledo DSC1” system in 150 μL (4.5 mm diameter) Pt crucibles. For each run, the temperature was increased from 25 up to 700 °C under Ar at atmospheric pressure with a slew rate of 10 °C/min .

Ohmic contacts have been electrically characterized using a four probes equipment and SCR values have been extracted from current-voltage (I-V) measurements made at room temperature with a “keitley 2400” on circular Transfer Length Method (c-TLM) patterns.

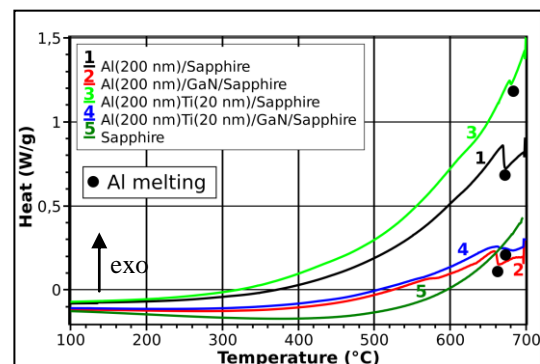


Figure 2 DSC characterization of bare sapphire, Al(200 nm) and Al(200 nm)Ti(20 nm) on GaN epilayer and Sapphire bare substrate.

3 Results and discussion

3.1 DSC measurements DSC characterization results are shown on Fig. 2 and 3. Results on bare sapphire

are the same as for empty crucibles. As expected, no reaction happens in sapphire within this temperature range. 100 % Al samples, both on bare Sapphire and on GaN epilayer, exhibit one endothermic peak at 660 °C which obviously can be attributed to Al melting. This gives an illustration of the sensitivity of the experiments, since the sample contains only <math><10\ \mu\text{g}</math> Al on $\sim 40\ \text{mg}$ Sapphire .

Adding a 20 nm thick Ti layer in the system, the Al melting peak is still observable but weaker, on both GaN and bare sapphire substrates. It means that Al has already started to react at temperatures below Al melting, but the system is not sensitive enough to detect the reaction heat.

For samples with Al(200 nm) and Ti(50 or 100 nm), a smooth exothermic peak appears in the range 420-500°C. For Ti(100 nm), another exothermic peak appears near 660 °C.

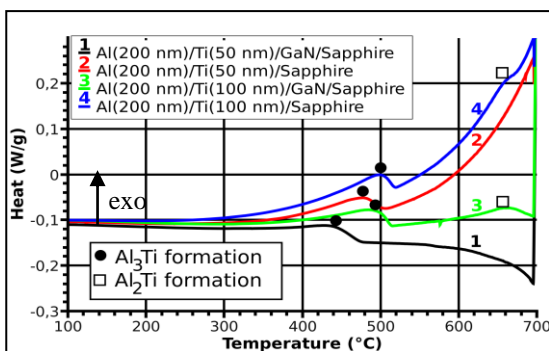


Figure 3 DSC characterization of Al(200 nm)/Ti(50 nm) and Al(200 nm)/Ti(100 nm) on GaN epilayer and Sapphire bare substrate.

Since these peaks are observed with and without GaN layer, they have to be related to reactions between Al and Ti. In agreement with the Ti-Al binary phase diagram (Fig. 1) and XRD measurements, we attribute these peaks to the formation of Al_3Ti and Al_2Ti compounds.

The Al_3Ti related peak happens at temperature lower than Al melting. It means that Al_3Ti results from solid-solid reaction, with no precise temperature threshold. The peak position is therefore influenced by the reaction kinetics, hence by the experimental temperature ramp slope.

For Ti(50 nm), the Al-Ti stack is Al-rich and the whole Ti is consumed first with some Al remaining unreacted.

In contrast, for Ti(100 nm), the stack is Ti-rich and the whole Al(200 nm) reacts to form Al_3Ti . There is more reactive material and, for the same temperature slope, it takes more time to achieve complete reaction. This is why the exothermic Al_3Ti peak shifts towards higher temperatures. Then, the excess Ti reacts with Al_3Ti to form Al_2Ti .

3.2 SCR measurement Since it seems clear that $\text{Al}_3\text{Ti}/\text{GaN}$ interface is responsible for the low SCR, and since Al_3Ti formation starts below 500°C, we have investigated the evolution of the SCR for lower temperature annealing. Ohmic contacts have been fabricated on optimized Al(200 nm)/Ti(50 nm) structures on n^+ -GaN. Room tem-

perature SCR values have been extracted from (I-V) measurements on circular Transfer Length Method (c-TLM) patterns. The contact starts to be ohmic around 450°C and the SCR stays in the mid $10^{-5}\ \Omega\cdot\text{cm}^2$ up to 650°C (Fig. 4).

4 Conclusion DSC characterizations of Ti-Al systems on GaN epilayer and bare sapphire substrates tend to show that the Al_3Ti and Al_2Ti compounds are formed through solid-solid reactions, with Al_3Ti formation starting below 500°C. Al(200 nm)/Ti(50 nm) contacts on n^+ -GaN yield SCR values in the mid $10^{-5}\ \Omega\cdot\text{cm}^2$ in the whole annealing temperature range 450- 650 °C.

The possibility to get reliable ohmic contacts on n-type GaN with such low annealing temperature may pave the way towards simpler and cheaper device processing, in which ohmic and Schottky contacts could be annealed together.

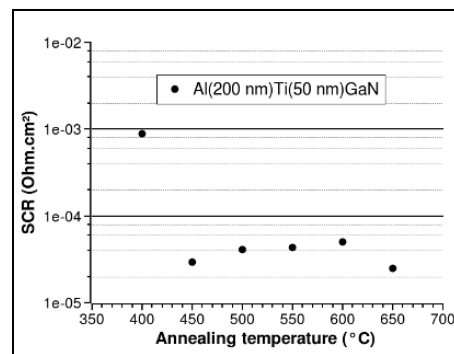


Figure 4 Evolution of the SCR with the annealing temperature of a Al(200 nm)/Ti(50 nm) on n^+ -GaN contact.

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