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Farah Laariedh, Mihai Lazar, P. Cremillieu, J. Penuelas, J-L Leclercq, et al.. The role of nickel and titanium in the formation of ohmic contacts on p-type 4H–SiC. Semiconductor Science and Technology, 2013, 28 (4), 10.1088/0268-1242/28/4/045007. hal-01627844

HAL Id: hal-01627844

https://hal.science/hal-01627844

Submitted on 9 May 2019

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The role of nickel and titanium in the formation of ohmic contacts on p-type 4H-SiC

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Keywords: Silicon Carbide, Ohmic contact resistance, nickel silicide, titanium silicon carbide, SIMS, EDX and XRD.

Abstract. The formation of low resistivity ohmic contacts to p-type 4H-SiC is achieved. Transfer Length Method (TLM) based-structures were fabricated on 0.8 μ m-thick epitaxial p-type Silicon Carbide (4H-SiC) layers. TLM metal patterns were obtained by a lift-off procedure and electron beam deposition of Ni, Ti and Al. The electrical properties of the contacts were examined using current/voltage measurements. Contact resistivity as a function of annealing was investigated over the temperature range from 700°C to 1000°C. The lowest contact resistivity of $1.5\times10^{-5}~\Omega.cm^2$ was obtained for Ni/Ti/Al/Ni contact after annealing at 800°C for 90s. Using Secondary Ion Mass Spectrometry (SIMS), Energy-Dispersive X-Ray spectroscopy (EDX) and X-Ray Diffraction (XRD) measurements we quantitatively and qualitatively determined the formation and the nature of the ohmic contact to p-type SiC.

PACS: 85.40.Ls, 73.40.Cg, 68.35.bd

1. Introduction

The inherent properties of silicon carbide (SiC) such as wide bandgap, high thermal conductivity, and high breakdown voltage make it a very promising material for high power, high temperature and high-frequency device applications where Si and GaAs devices cannot be used. One of the most critical issues currently limiting the device processing is the manufacturing of reliable and low resistance ohmic contacts on silicon carbide [1-3]. Since the work function difference between metals and p-type SiC is extremely large, it is very difficult to form ohmic contacts. To answer to this problem, it is necessary to choose metals with low Schottky barrier and to overdope p-type SiC layer close to the metal contact. To form such narrower bandgap interface SiC/Contact, many materials have been examined. Among them, nickel, titanium and aluminium have attracted more attention.

Ni-Ti alloy contacts which have been successfully used in the fabrication of ohmic contacts on n-type SiC layers [4] present specific contact resistances on p-type SiC layers in the order of 10^{-3} $\Omega.\text{cm}^2$ [5] which are not enough low in order to fabricate reliable power or high temperature SiC devices. To improve the quality of these contacts, aluminium based materials such as Ti/Ni/Al, Ni-Al and Al-Ti [6-9], have been used resulting in specific contact resistances lower than $1.10^{-4}_{-}\Omega.\text{cm}^2$. For the Al-Ti alloy, the ohmic behaviour is obtained but remains very sensitive to the quantity and

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stability of the aluminium layer. The composition (in weight) of Al 90 % - Ti 10 % yielded to the lowest specific resistance of $10^{-6}\,\Omega.\text{cm}^2$ however this result was not reproducible [10,11]. On the other hand the composition Al (70 %) - Ti (30 %) represents the best choice for a good and reproducible contact with a specific resistance of the order of $10^{-5}\Omega.\text{cm}^2$ [12,13].

In such high Al-content contacts, overdoping of the SiC/metal contact interface is obtained producing a heavily p-type doped region and yielding to low resistance contacts [11,14]. Al seems to create intrusions into the SiC, as its diffusion is still very difficult ¹¹. It has also been noted the possibility of thermal exo-evaporation of some Al during annealing performed at around 1000° C [15]. Thus, other metals have to be added to the interface in order to improve in depth-penetration of dopants into the SiC. Titanium is added to lower the extremely high thermodynamic driving force for oxidation of Al [16]. Alternative materials such as co-evaporation of TiC and sputtered TiW have been studding to form ohmic contacts on high doped p-type SiC obtaining specific ohmic resistance of $2\times10^{-5} \,\Omega.\text{cm}^2$ [17].

In this article we present the results of Al/Ti/Ni-based low resistive ohmic contacts to p⁺-type epilayers of 4H-SiC. We selected Ni as the key contact element. Ni was reported to react at low temperatures as 500°C with SiC by forming Ni₂Si silicide [18,19]. Ohmic contacts realized at low temperatures have a particular interest in the development of SiC MOSFET technology. Ti was added to the Ni/Al contacts to prevent the formation of unreacted interfacial carbon atoms [14,20]. Our study proposed to identify the role of each element and the phase formed at the metal/semiconductor interface by complementary electrical and physic-chemical analyses. "This paper presents our extended results on the metallization process in order to obtain reliable ohmic contacts operating up to 300°C. The first results have been reported in Ref. [21].

2. Experimental

Transfer Length Method (TLM) structures, were fabricated on 0.8 μm -thick epitaxial p-type ($N_A=3$ to $4.10^{19}~cm^{-3}$) layers isolated from the substrate by a 12 μm thick n-type epilayer ($N_D=5.10^{15}~cm^{-3}$ - the epitaxial data were furnished by the epilayer supplier). The TLM structures were also isolated in lateral by forming 2 μm deep trenches realized by reactive ion etching (RIE) with SF_6/O_2 . After degreasing in organic solvents, rinsing in de-ionized water (DI) and cleaned with standard RCA solution, the samples were finally dipped in BOE (Buffered Oxide Etchant) solution for 2 min at room temperature.

TLM patterns were then defined by lift-off of Ni,Ti and Al layers deposited on the SiC substrates by electron-beam evaporation in a high vacuum chamber where the base pressure was below 1.10^{-7} mbar, and the pressure during deposition was below 5.10^{-7} mbar. Thicknesses of the metal layers are given in table 1 and were double checked via quartz microbalance and X-ray reflectivity measurements (not shown here).

The contacts were annealed under Ar atmosphere with JIPELEC rapid thermal annealing (RTA) furnace on a graphite holder. The annealing procedure is performed in several steps. The first one consists in a relatively low temperature ramping up to 350°C, then the temperature is set to the contact formation temperature, varying from 700 to 1000°C, landing at this temperature during 90s. Prior to metal annealing the furnace was cleaned with successively vacuum purges.

Electrical characterization after annealed contacts was performed by current-voltage (I-V) measurements. The specific contact resistances were extracted by a Transfer Length Method (TLM), with $80x500 \,\mu\text{m}^2$ metal patterns with spacing distances of 25, 35, 45, 55, 65 and 75 μm . The distance from the TLM metal patterns to the etched mesa edges is $20\mu\text{m}$ which is insignificant compared to the metal patterns width ($500 \,\mu\text{m}$) and allows us to consider TLM one-dimensional model and to omit the lateral current crowding [12].

Using Secondary Ion Mass Spectrometry (SIMS) with a CAMECA IMF and an O^{2+} primary ion beam, Energy-Dispersive X-Ray spectroscopy (EDX) with a SEM Philips CM120 and X-ray Diffraction measurements before and after annealing, we investigate qualitatively and quantitatively the formation of the contacts and their evolution at the SiC/contact interface. X-ray diffraction measurements were performed with a diffractometer equipped with a rotating anode operating at 9 kW. The X-ray were monochromatized using a double Ge(400) crystal which selects the Cu kalpha1 radiation (wavelength = 1.5406\AA).

Table 1. Thicknesses of Ni, Al, and Ti layers and acceptor concentrations in SiC substrates.

Composition of the	Thickness of the		
metal contact	metal contact (nm)		
Ti/Al/Ti/Ni	5/60/30/100		
Ni/Ti/Al	25/50/300		
Ni/Ti/Al	12.5/25/150		
Ni/Ti/Al/Ni	12.5/50/300/12.5		
Ni/Ti/Al/Ni	10/40/240/10		
Ni/Ti/Al/Ni	5/20/120/5		

3. Results and discussion

First, we have noted that despite the high doping level at 3.10¹⁹ cm⁻³ of our p-type 4H-SiC layers, the as-deposited metal contacts formed a Schottky barrier. After 90s annealing at 700 °C of the contacts, typical I-V characteristics are given in Figure 1 for the three families of the contact alloys presented in Table1. A linear I-V characteristic can be seen indicating that the contact becomes ohmic, only if the Ni layer is present at SiC surface for the temperatures as low as 700°C.

For the metallic contacts with Al on top, the presence of an on-surface insulating layer has been observed whatever the annealing temperature. This makes difficult the measure of the contacts and the electric characterization which can be only made once this layer is removed by mechanical action (we scratch these contacts with the point) or by a long Ar/H₂ RIE plasma. To solve this problem, the Ni/Ti/Al contact was capped with a top layer of Ni avoiding the oxidation of the aluminium or other phenomenon responsible of this insulating layer in surface.

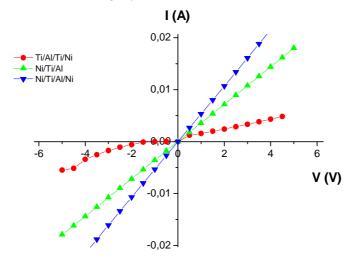


Figure 1. Typical I-V characteristics of the contacts for the three different families of the used alloys obtained after 90s annealing at 700°C.

Regarding these first experiments which show after annealing a non ohmic contact with the Ti/Al/Ti/Ni alloy and the presence of an insulated layer on the top of the contacts with Ni/Ti/Al initial stacking sequence, we selectively focused on Ni/Ti/Al/Ni contacts by studying the effects of the annealing temperature (figure. 2). The dependence of the electrical properties of the Ni/Ti/Al/Ni contacts on the annealing conditions was studied over the 700°C to 900°C temperature range. The specific resistance, and then the contact resistivity, was observed to vary with the annealing temperature. The specific resistance decreases with increasing annealing temperature until 800°C, then it increases with the temperature indicating, probably, the deterioration of the contact. The lowest contact resistance of $1.5 \times 10^{-5} \,\Omega.\text{cm}^2$ was obtained at 800°C.

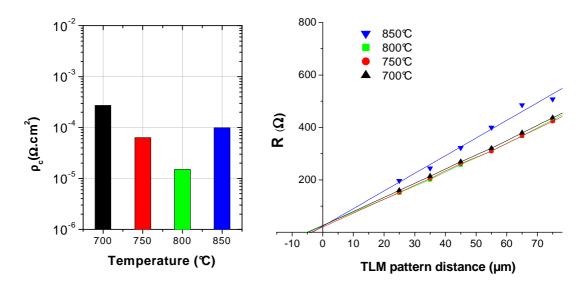


Figure 2. Resistance extracted versus distance between TLM pads of the Ni(10) /Ti(40) /Al(240) /Ni (10nm) contacts and dependence of the specific contact resistance from annealing temperatures at 700 to 850°C.

Considering the capping effect of Ni on top of the Ni-Ti-Al contacts, it is important to note that a thickness of 5 nm is not sufficient to avoid the presence of on-surface insulating layer. The resistances extracted from the extreme patterns of the TLM are not aligned with the inner ones as those presented in figure 2. Insulated layers were formed at the edge of TLMs metal patterns close to the etched mesas.

Then physico-chemical studies have been conducted to identify the chemical composition (and then the origin) of this insulating layer at the top contacts. These physico-chemical analyses allow also us to identify the phases formed at the SiC interface which could be considered as responsible of the ohmic behaviour of our contacts.

At first, the contact element profile was investigated by SIMS before and after annealing at 800°C. Before the annealing we can see as expected the successive metallic elements Ni(5)/Ti (20)/Al(120)/Ni(5nm) stacking from the surface to the SiC interface corresponding to their respective deposited position (figure. 3a).

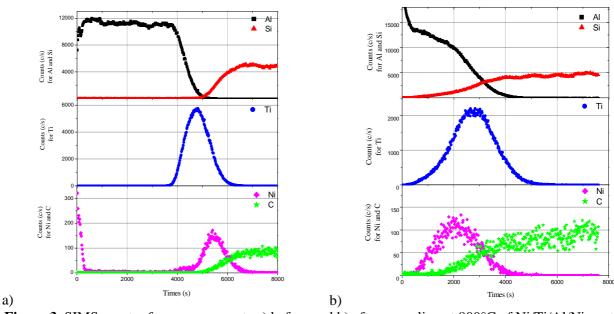


Figure 3. SIMS spectra for measurements a) before and b) after annealing at 800°C of Ni/Ti/Al/Ni contacts on 4H-SiC samples.

The RTA process leads to the redistribution of the metallic elements into the SiC (figure. 3b). It shows the formation of a layered contact structure having two clearly regions. The top surface is enriched with Al, the Al profile geometry suggesting a possible evaporation in surface. Al, Ni and Ti have penetrated in depth in the SiC. This interacting zone close to the SiC interface should be significative of the probable formation of metallic silicides and/or carbides alloys such as Ni₂Si, TiC and Ti₃SiC₂ which can favour the ohmic behaviour. We should also note the absence of a carbonic layer at the SiC interface, no peak of the C is detected by our SIMS measurements and the plateau profile of the C is escorted by the Si plateau profile. The carbonic layer at the SiC interface is often reported to be responsible for the high values of the specific ohmic contact resistivity [14]. This must be correlated with the presence of the Ti which is a key-element for the formation of Ti-based carbides. Compared to the results presented by Vassilevski et al [7], our profiles of Ti and C are not correlated. We can therefore suppose that Ti-Si carbide have been formed instead of TiC. As mentioned by Johnson et al [9], Ti₃SiC₂ ternary phase presents a significant effect in the formation of ohmic contact to p-type SiC by forming a narrow-gap interfacial alloy reducing the Schottky barrier height at the metal-SiC interface.

On the other hand we remark the Ni profile evolution approaching to that of the Si which can be explained probably by the formation of Ni₂Si. Our electrical measurements on TLMs structures show how important the presence of the Ni at the metal-SiC interface can be for the formation of ohmic contacts for annealing temperatures as low as 700°C. The Ni₂Si alloy already mentioned to be formed at this low temperature [18,19], seems to play a role in the formation of ohmic contact on p-type SiC as for the contacts on n-type SiC.

The composition of the intermetallic phases was studied by X-ray diffraction analysis (XRD) in order to confirm the presence of these alloys at the SiC interface. The X-ray spectra of Ni/Ti/Al/Ni films deposited on 4H-SiC before and after annealing at 800°C are shown in figure 4. Before annealing, several Bragg reflections are identified corresponding to the SiC (0001) substrate and the non-alloyed bulk phase of Ti, Al and Ni. Epitaxial relationships of the deposited metals were not investigated. After high-temperature annealing at 800°C, we can observe the presence of numerous peaks revealing the formation of several intermetallic phases such as Ti₃SiC, Ni₂Si, Al₂Ti or NiAl₃. These measurements are in good agreement with our previous results from SIMS, these intermetallic phases, especially Ti₃SiC and Ni₂Si, seem to favour the formation of the ohmic contact.

Moreover, the creation of Al-Ti and Al-Ni phases limit the presence of elementary Al on top of the surface and then its oxidation leading to the increase of contact resistance.

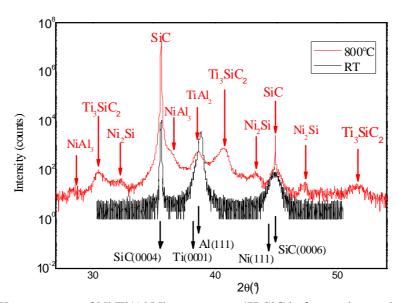


Figure 4. X-ray spectra of Ni/Ti/Al/Ni contacts on 4H-SiC before and annealed at 800°C.

This oxidation which creates the insulating layer on the top of the contacts was also confirmed by EDX chemical analyses. The concentrations of every constituting metal contact elements are given in table 2 before and after annealing. Surprisingly, we have found after annealing the presence of an

important amount (up to 29 at%) of O₂. Whatever, this oxygen presence did not influence the ohmic property of the Ni/Ti/Al/Ni contacts as we showed by electrical measurements.

Table 2. EDX results after annealing Ni(5nm)/Ti(20nm)/Al(120nm)/Ni(5nm) contacts on 4H-SiC

samples.								
	Before annealing		After annealing Ar at 3.3 10 ⁻³ mbar		After annealing under Ar at 10 ³ mbar			
	w%	at%	w%	at%	w%	at%		
С	8.82	19.70	4.42	8.50	7.04	15.82		
O	0.00	0.00	20.09	28.98	2.99	5.04		
Al	34.86	34.65	45.40	38.84	25.69	25.72		
Si	39.83	38.02	27.62	22.70	47.52	45.70		
Ti	1.00	0.56	0.00	0.00	0.00	0.00		
Ni	15.49	7.07	2.46	0.97	16.77	7.72		

Nevertheless the amount of O_2 in our contacts was decreased to 5 at% (table 2) by increasing the Ar pressure from 3.3 10^{-3} mbar to one atmosphere (10^3 mbar) during our RTA process.

We remark that the amount of the Ni detected by the EDX analyses drastically decreases after annealing in Ar at 3.3 10⁻³ mbar while the Al concentration increases. The formation of the insulated layer in surface prevents the detection of the Ni in depth by the EDX teardrop-shaped volume. Nevertheless after annealing under Ar at one atmosphere (10³ mbar) without insulated layer in surface, the amount of the Ni found by EDX is close to the concentration before annealing. Concerning the concentration of Ti the values we obtained are very small before and after annealing due to its deeper localization compared with Ni (as showed by SIMS analyses), closer to the SiC interface after annealing and enough far from the EDX teardrop-shaped volume detection limit.

Considering our optimal ohmic contact configuration, with the Ni(10)/Ti (40)/Al(240)/Ni(10nm) stacking annealed at 800°C, finally a thermal stress-test has been applied between 25°C to 300°C. The contact reliability at high temperature is usually considered as the crucial factor determining the limitation of a contact system for power device applications. The experimental results are presented in Figure 5. We note that the measured specific contact resistances are higher that those reported in Figure 2. This is due to the experimental setup during which the TLM patterns were damaged during the probe tips manipulation (the contacts with the TLM patterns must be made and released for each measurement temperature). We preferred to not add a surmetallisation layer in order to characterize only our stacking annealed alloy

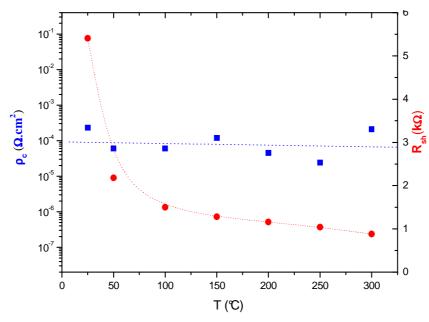


Figure 5. The dependence of the specific contact resistance and sheet resistance under the thermal stress for the Ni(10)/Ti(40)/Al(240)/Ni(10nm) contacts annealed at 800°C in Ar

As shown in the figure 5, the specific contact resistance did not varied under the thermal stress. This can be attributed to the formation of intermetallic phases which are stables up to 300°C.

We also observe a normal decrease of the sheet resistance R_{sh} due to the ionization of Al and thus to the increase of the holes concentration which is a typically behaviour of wide bandgap semiconductors with incomplete ionisation of the dopants at room temperature.

4. Summary

Low resistivity Ni/Ti/Al/Ni-based ohmic contacts on p-type doped SiC were investigated and discussed. The lowest contact resistivity of $1.5 \times 10^{-5} \ \Omega.\text{cm}^2$ has been obtained after annealing at 800°C for 90s in argon atmosphere.

The results of this study show that the adding of Nickel into the Ti-Al contact composition at the SiC interface is critical to obtain good ohmic contacts with low access resistance limiting the potential oxidation of the elementary Al.

The rapid thermal annealing of multilayer Ni/Ti/A1/Ni metal composition led to the formation of Ni₂Si, Ti₃SiC₂, Al₂Ti and NiAl₃ intermetallic phases. This ohmic contact is thermally stable up to 300° C.

5. Acknowledgements

The authors would like to acknowledge the Linkopings Universitet represented by Dr Jawad ul Hassan and Prof Anne Henry for epitaxial growth. The authors also wish to thank Dr Christiane Dubois from INL laboratory for SIMS analysis, Dr Davy Carole and Stéphane Berckmans from LMI laboratory for EDX analysis, the financial support by the USAR-ANR, is gratefully acknowledged.

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