A Study on the Chemistry of Epitaxial Ti3SiC2 Formation on 4H-SiC Using Al-Ti Annealing

Tony Abi-Tannous, Maher Soueidan, Gabriel Ferro, Mihai Lazar, Berangère Toury, Marie-France Beaufort, Jean François Barbot, Jose Penuelas, Dominique Planson

A study on the chemistry of epitaxial Ti_3SiC_2 formation on 4H-SiC using Al-Ti annealing

T. Abi-Tannous[1,a*], M. Soueidan[1,b] , G. Ferro[2,c] , M. Lazar[1,d] , B. Toury[2,e], M.F. Beaufort[3,f] , J.F. Barbot[3,g] , J. Penuelas[4,h] and D. Planson[1,i]

[1]Université de Lyon, CNRS, Laboratoire Ampère, INSA-Lyon, UMR 5005, F-69621, France

[2]Université de Lyon, CNRS, Laboratoire des Multimatériaux et Interfaces, UMR 5615, F-69622, France

[3]Institut Pprime CNRS - Université de Poitiers - ENSMA - UPR 3346 Département Physique et Mécanique des Matériaux SP2MI - 86962 Futuroscope Chasseneuil Cedex, France

[4]Université de Lyon, Institut des Nanotechnologies de Lyon, UMR CNRS 5270, 69134 ECULLY Cedex France

[a]tony.abi-tannous@insa-lyon.fr, [b]maher.soueidan@insa-lyon.fr, [c]gabriel.ferro@univ-lyon1.fr, [d]mihai.lazar@insa-lyon.fr, [e]berangere.toury-pierre@univ-lyon1.fr, [f]marie.france.beaufort@univ-poitiers.fr, [g]jean.francois.barbot@univ-poitiers.fr, [h]jose.penuelas@ec-lyon.fr, [i]dominique.planson@insa-lyon.fr

Keywords: Ti-Al alloy, MAX phase, Ti_3SiC_2, ohmic-contact, p-type 4H-SiC

Abstract. In order to form Ti_3SiC_2 on 4H-SiC(0001) 8°-off, 200 nm of $Ti_{30}Al_{70}$ was deposited onto SiC substrates by magnetron sputtering from pure $Ti_{30}Al_{70}$ targets. The samples were then annealed at 1000°C for 10 min under Ar atmosphere in a Rapid Thermal Annealing (RTA) furnace. Structural analyses reveal the formation of epitaxial hexagonal Ti_3SiC_2 (0001) oriented. Elemental analyses show that high amount of Al and O elements are present inside the deposit. Obviously, the formation of Ti_3SiC_2 is accompanied by parasitic Al oxide, probably due to some unwanted oxygen residual in the RTA chamber. By using proper backing steps before the annealing, the deposit is not anymore composed of only Ti_3SiC_2 but accompanied with other compounds (Al_3Ti, and Al). On the oxide-free sample, the specific contact resistance ρ_c of the Ti_3SiC_2 based contact on p-type 4H-SiC (having $N_a = 2\times10^{19}$ cm^{-3}) was measured to be as low as 6×10^{-5} Ω.cm^2.

Introduction

To achieve reliable, high quality 4H-SiC devices, low resistance ohmic contacts on SiC (n- or p-type) are necessary. This is known to be especially difficult on *p*-type SiC. Rather good results have been obtained from high-temperature annealed Ti and Al-containing alloys [1-5]. The reason why these alloys display low contact resistance is still under discussion though the beneficial effect of the resulting MAX phase Ti_3SiC_2 is often suggested [6,7]. This material has a very interesting combination of metallic properties such as high thermal and electrical conductivity and ceramic properties such as being resistant to oxidation and thermal shock [8], with an excellent chemical compatibility with SiC. Epitaxial Ti_3SiC_2 on on-axis and 8°-off 4H-SiC after Al-Ti annealing was already reported [9,7] but the chemical paths leading to its single formation are not well understood. For instance, where do Al and Si excesses go? Is there any amorphous oxide formation?

The goal of this study is to try answering these questions while finding conditions for forming Ti_3SiC_2 on 4H-SiC(0001) 8°off after annealing of Ti-Al based stacking.

Experimental section

The samples used for this study are Si face 4H-SiC(0001) substrates 8° disoriented. Before metallization, the samples are chemically cleaned to remove any surface pollution. This implies acetone and ethanol ultrasonic degreasing for 5 min each, followed by H_2SO_4: H_2O_2 (75: 25) for 10 minutes and finally HF acid diluted at 5% for 4 min, before rinsing with deionized water. After cleaning, 200 nm of $Ti_{30}Al_{70}$ was deposited onto SiC substrates by magnetron sputtering from pure

$Ti_{30}Al_{70}$ targets in a high vacuum system. The deposition was carried out with an Ar constant pressure (5×10^{-3} mbars) at room temperature. The samples were then annealed at 1000°C for 10 min under Ar atmosphere in a rapid thermal annealing furnace (heating rate of about 20°C/s) [9]. Some experiments were performed on p-type 4H-SiC epitaxial layers, with doping concentration of 2×10^{19} at/cm^{-3}, in order to allow determination of the Specific Contact Resistance (SCR) using the Transfer Length Method (TLM) structure.

Identification of reaction products

Figure 1-a shows X-ray diffraction (XRD) θ-2θ scan of a typical sample annealed in these conditions. As seen, the diffraction peaks unambiguously reveal the formation of the hexagonal Ti_3SiC_2 structure which is in epitaxial relation with the substrate. The rocking curves obtained on the (0008) diffraction planes of the Ti_3SiC_2 phase (Figure 1-b) present a full width at half-maximum (FWHM) of 0.4° showing the good crystallinity of the film. Using X-ray photoelectron spectroscopy (XPS) analyses, the presence of Al was also detected in high amount on the surface, but its depth profile was associated with the presence of O element (Figure 2). Such surface oxide layer was not seen from XRD measurements probably because under amorphous state.

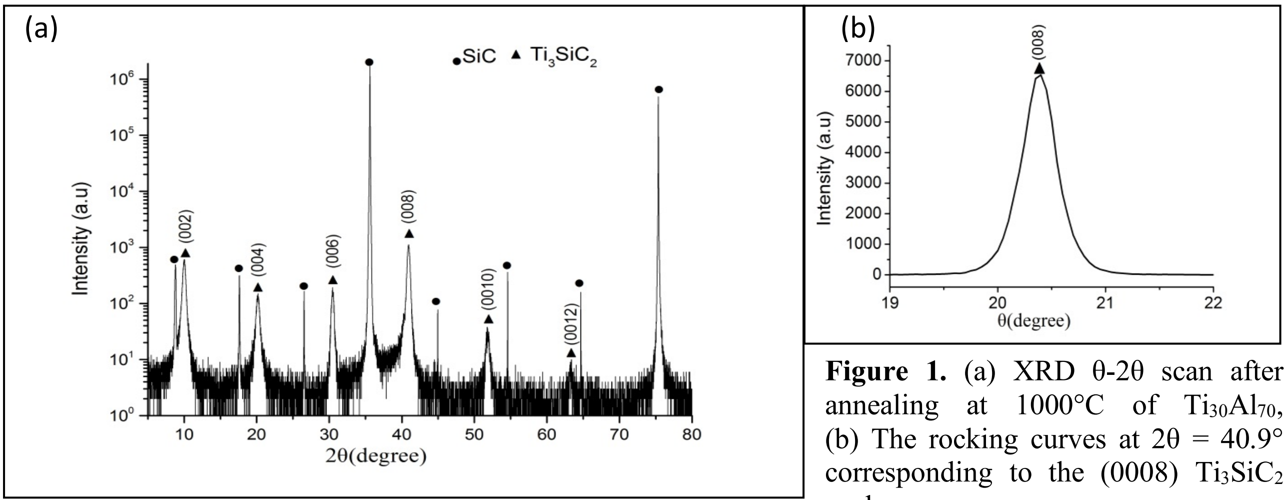

Figure 1. (a) XRD θ-2θ scan after annealing at 1000°C of $Ti_{30}Al_{70}$, (b) The rocking curves at 2θ = 40.9° corresponding to the (0008) Ti_3SiC_2 peak.

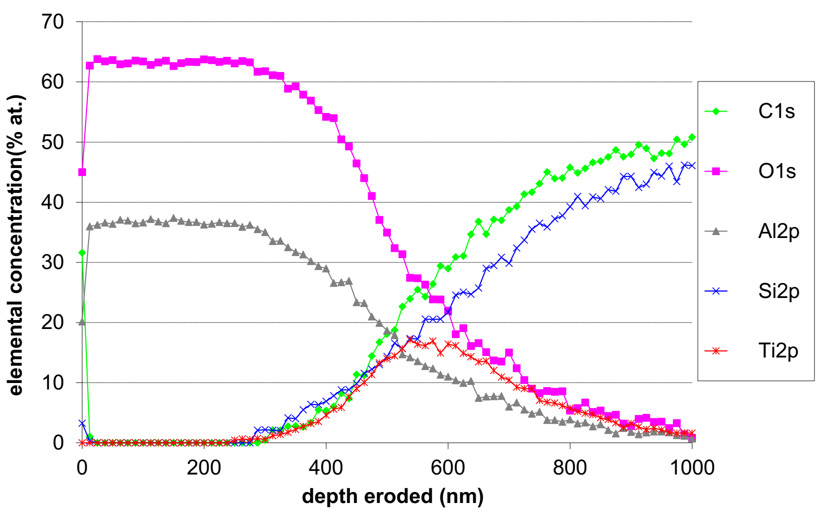

Figure 2. XPS depth profile of C, O, Al, Si and Ti of the TiAl contacts onto 4H-SiC annealed at 1000°C for 10 min.

In order to confirm these results, transmission electron microscopy (TEM) investigations were carried out. Figure 3 displays a low magnification bright field (BF) image of a typical region of an as-annealed sample. This general view shows that the 4H-SiC substrate is entirely covered by a Ti_3SiC_2 layer with varying thickness from ~95 to 140 nm. On top of this is found an almost continuous layer which was attributed to amorphous to polycrystalline Al oxide (probably Al_2O_3).

As a matter of fact, the formation of Ti_3SiC_2 is accompanied by parasitic Al oxide, probably due to some oxygen residual in the RTA chamber. For ohmic contact, such oxide layer is obviously unwanted and conditions shall be found for avoiding its formation. That is why advanced baking steps were implemented before the annealing. The effects of such baking were directly seen from the XRD measurements (Figure 4). Ti_3SiC_2 is not the only phase detected and its formation is now accompanied by Al_3Ti, and pure Al. As a result, oxygen seems to play a key role during the Ti-Al/SiC interaction for obtaining only one Ti-based phase (Ti_3SiC_2). This is probably what was happening in the work of A. Drevin-Bazin [9]. The following "globally" chemical reactions are proposed to summarize the results obtained:

Without oxygen: $20Al + 9Ti + 2SiC \rightarrow Ti_3SiC_2 + 6Al_3Ti + 2Al + Si$

With oxygen: $14Al + 6Ti + 4SiC + 25/2O_2 \rightarrow 2Ti_3SiC_2 + 7Al_2O_3 + 2SiO_2$

Apparently, oxygen is "pumping" preferentially the Al atoms from the Al-Ti alloy so that the system moves towards the single Ti_3SiC_2 phase instead of forming a mixture with Al_3Ti.

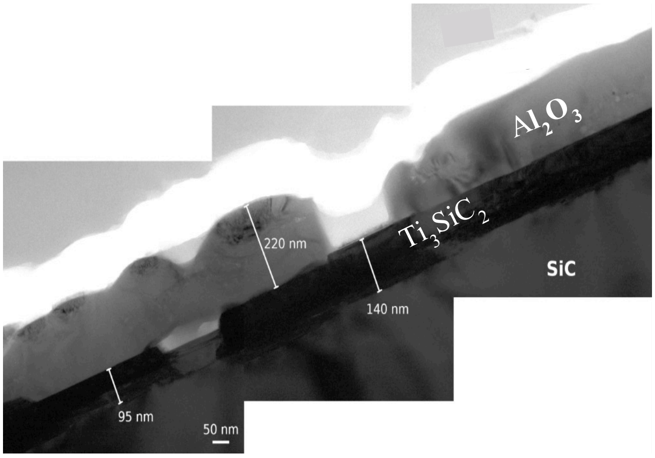

Figure 3. Cross-sectional TEM image of the same sample as in figure 1-a. Ti_3SiC_2 covers completely the surface of the SiC substrate and is itself covered by an Al oxide layer.

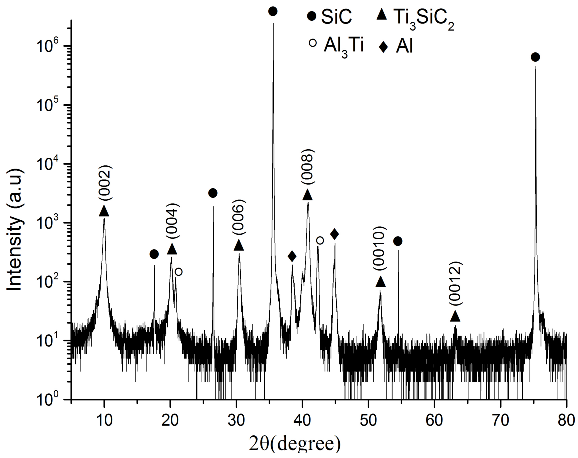

Figure 4. XRD pattern of the TiAl contacts onto 4H-SiC annealed at 1000°C for 10 min with proper baking of the system.

Electrical characterization

The geometric patterns for the TLM (Transfer Length Method) measurements were obtained through a photolithographic procedure. The tested layer was laterally isolated by RIE etching of the SiC forming mesa structures. The p-type layers are also insulated vertically by the p/n junction. The commercially Al-etch at 60°C was used for etching the metal patterns. After such procedure, the TLM pattern consists of multiple rectangular electrodes with increasing spacing of 6, 10, 20, 40, 80 and 120 µm. Using a 4-point probe method, the I-V characteristics are plotted as function of the contact spacing for a 200 nm-thick $Ti_{30}Al_{70}$ layer annealed at 1000°C during 10 min (see Figure 5).

As seen for all the spacing, the I-V curves are perfectly linear showing again the ohmic character of the Ti_3SiC_2-based contact for p-type 4H-SiC. The total resistances, deduced from the curves of figure 5 are plotted as function of spacing between the contact pads (Figure 6). In the configuration used, the curve showing the total resistance according to the distance between the metal pads is linear. From figure 6 it can be inferred that the specific contact resistance is about 6×10^{-5} $\Omega.cm^2$. This value is among the best compared to the state of the art [1-5].

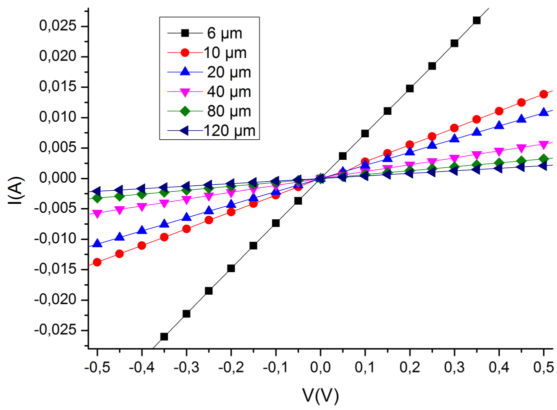

Figure 5. I-V characteristics of the sample for different distances between the contact pads of the TLM structure.

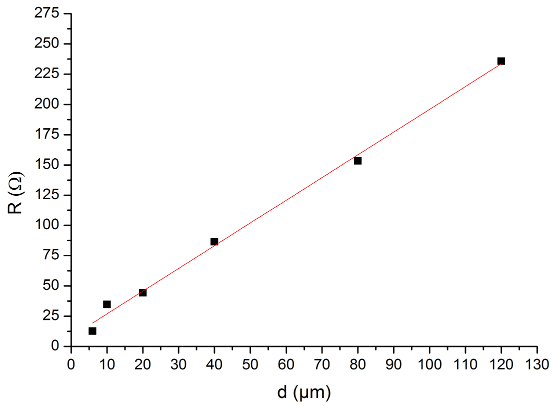

Figure 6. Evolution of resistance as a function of the distance between the contact pads for the same sample as in figure 5.

Summary

We have shown that it is possible to form epitaxial Ti_3SiC_2 onto 4H-SiC (0001) 8°-off from 200 nm of $Ti_{30}Al_{70}$ alloy, deposited by sputtering and annealed in a rapid thermal annealing at 1000°C during 10 min. TEM images show that Ti_3SiC_2 covers completely the surface of the SiC substrate and is itself covered by an Al oxide layer. By using proper baking steps before the annealing, the results are clearly different. Several compounds (Ti_3SiC_2, Al_3Ti, and Al) are then detected. On the oxide-free sample, the specific contact resistance of the Ti_3SiC_2 based contact on p-type 4H-SiC (having $N_a = 2\times10^{19}$ cm^{-3}) was found to be $\rho_c = 6\times10^{-5}$ Ω.cm^2. Our results are among the best compared to the state of the art.

References

[1] F. Roccaforte, A. Frazzetto, G. Greco, F. Giannazzo, P. Fiorenza, R. Lo Nigro, M. Saggio, M. Leszczynski, P. Pristawko, V. Raineri, Applied Surface Science 258 (2012) 8324– 8333.

[2] F. A. Mohammad, Y. Cao, K.-C. Chang, and L. M. Porter, Jpn. J. Appl.Phys. 44, 5933 (2005).

[3] R. Konishi, R. Yasukochi, O. Nakatsuka, Y. Koide, M. Moriyama, and M. Murakami, Mater. Sci. Eng., B 98, 286 (2003).

[4] S. Tsukimoto, K. Nitta, T. Sakai, M. Moriyama, and M. Murakami, J.Electron. Mater. 33, 460 (2004).

[5] N. Thierry-Jebali, A. Vo-Ha, D. Carole, M. Lazar, G. Ferro, D. Planson,A. Henry and P. Brosselard, Appl. Phys. 102, 212108 (2013).

[6] S. Tsukimoto, K. Ito, Z. Wang, M. Saito, Y. Ikuhara, and M. Murakami, Mater. Trans. 50, 1071 (2009).

[7] Z. Wang, S. Tsukimoto, M. Saito, K. Ito, M. Murakami, and Y. Ikuhara, Phys. Rev. B 80, 245303 (2009).

[8] P. Eklund, M. Beckers, U. Jansson, H. Högberg, and L. Hultman, Thin Solid Films 518, 1851 (2010).

[9] A. Drevin-Bazin, J.F. Barbot, M. Alkazaz, T. Cabioch, M.F. Beaufort, Appl. Phys. Lett. 101, 021606 (2012).