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Single-step synthesis process of Ti_3SiC_2 Ohmic contacts on 4H-SiC by sputter-deposition of Ti

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We report a single-step procedure for growth of Ohmic Ti_3SiC_2 on 4H-SiC by sputter-deposition of Ti at 960 °C, based on the Ti-SiC solid-state reaction during deposition. X-ray diffraction and electron microscopy show the growth of interfacial Ti_3SiC_2 . The as-deposited contacts are Ohmic, in contrast to multistep-processes with deposition followed by rapid thermal annealing. This procedure also offers the possibility of direct synthesis of oxygen-barrier capping layers before exposure to air, potentially improving contact stability in high-temperature and high-power devices.

Keywords: Silicon carbide, MAX phase, Physical vapor deposition, high temperature

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Silicon carbide holds a combination of useful properties,¹ e.g., wide band gap, high breakdown electric field strength, high thermal conductivity and chemical inertness, making it ideal for electronic devices for high temperature and high power applications. One of the most basic electronic elements in such devices is a suitable Ohmic contact. To that end, Ti/Al based contacts are widely studied for 4H-SiC.²⁻⁷

The synthesis method of this class of Ohmic contacts requires a post-deposition process with rapid thermal annealing at around 950°C. This process results in the formation of new phases in the contact, mainly Ti_3SiC_2 and Ti_3Al . Transmission electron microscopy showed that Ti_3SiC_2 grows at the interface. Therefore, it is the main reason for Ohmic properties.⁸⁻¹⁰ Moreover, first-principles studies also attributed the efficient lowering of the Schottky barrier and corresponding Ohmic behavior, to the formation of Ti_3SiC_2 .¹¹⁻¹³

Ti_3SiC_2 is a member of the family of layered carbides and nitrides known as MAX phases^{14,15} where M is an early transition metal, A is an element from groups 12-16, and X is carbon or nitrogen. This family exhibits an unusual combination of metallic and ceramic-like properties¹⁶ such as high-temperature stability and high electrical conductivity. Ti_3SiC_2 thin films are commonly grown by physical vapor deposition, primarily sputtering from elemental^{17,18} or compound targets.¹⁹ However, growth of this phase on 4H-SiC was reported to still require high temperature rapid thermal annealing to exhibit Ohmic properties.²⁰ Transmission electron microscopy studies before and after the annealing process of Ti_3SiC_2 films showed that annealing resulted in a more ordered interface between the film and 4H-SiC.²⁰

Eliminating the annealing process-step, i.e., synthesizing as-deposited Ohmic contacts through a single-step process would be beneficial for the Ohmic contacts to SiC-based devices.²¹ In addition, this approach puts forward the possibility to directly synthesize oxygen-barrier capping layers after the main contact deposition without exposing the devices to air for a process-step like annealing, avoiding any risk of oxidation or contamination or any need for a cleaning-step. This can improve long-term

stability of devices using Ohmic contacts especially for operation at high temperature and in corrosive environment. Here, we report a straightforward procedure for that purpose, by deposition of Ti at high substrate temperature. The Ohmic contacts form during deposition because of the reaction between the sputter-deposited Ti and the substrate to form Ti_3SiC_2 .

The depositions were performed in an ultra-high vacuum stainless steel chamber with a base pressure lower than 1.3×10^{-6} Pa. The deposition sources were two sputtering targets, (Ti (99.995%) and Pt (99.99%)), 5.08 cm in diameter, run in power-regulated DC mode. We used the Pt target only for synthesis of capping layers. Temperature was calibrated before the series of depositions using a thermocouple placed at the substrate position. The substrates were mechanical grade n-type (10^{18} cm^{-3}) 4H-SiC, (0001), 4° off-axis, diced 10×10 mm in size. Prior to deposition, they were ultrasonically cleaned by acetone and isopropanol for 10 minutes each, blown dry in pure nitrogen and were directly inserted into the load-lock of the chamber. The sputtering gas was Ar with pressures of 0.32 and 0.1 Pa for Ti and Pt depositions, respectively. We used the minimum possible pressure of 0.1 Pa for deposition of Pt in order to eliminate film roughness. X-ray diffraction (XRD) was performed using a Philips PW 1820 instrument (Cu ($K\alpha$), θ - 2θ scan, aligned with the substrate (0004) peak). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were done in a LEO 1550 for surface imaging, chemical analysis and for film thickness measurement via cross sectional samples. We used 5 kV and 2 kV accelerating voltages for SEM and EDX, respectively. The choice of this low accelerating voltage for the latter method was made to obtain highly surface-sensitive mapping of C. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) studies were done in a Tecnai G2 TF20UT FEG microscope. Cross-sectional samples were first mechanically polished to a thickness of about 60 μm , followed by ion-beam milling with Ar^+ in a Gatan precision ion polishing system (PIPS) at 5 keV with a final polishing step at 1.5 keV of ion energies. For electrical

measurements, we deposited contacts on samples using a shadow mask, resulting in two distinct 4×10 mm² coated areas on the substrate with 1.2 mm distance in between. The shadow mask was made of 4H-SiC to rule out any potential reaction between the mask and the 4H-SiC substrate. To improve electric current spreading in the film, we deposited a 250 nm thick Pt layer on top of the main contacts before removing the shadow mask. Pt deposition was performed at room temperature to exclude any further influence of high temperature on the interface between the contact and 4H-SiC. In addition, it was done in the same chamber without breaking vacuum to prevent any oxidation and gas adsorption at the contact-capping layer interface. Current-voltage measurements (I-V) were performed using a Keithley 2601 source meter equipped with two removable gold-coated electrodes placed directly on the two separated contact areas on the substrate. In this set-up, the current flows through three different interfaces in each contact area on the substrate. These interfaces are removable contact-Pt, Pt-main contact and main contact-substrate. Any potential non-Ohmic behavior would only correspond to the latter since the first two are metal-metal contacts and are Ohmic. Therefore, this relatively simple measurement setup allows showing the Ohmic properties of the contacts. However, unlike a transmission line method²² (TLM), it does not allow to quantify the specific contact resistivity.

Figure 1 shows the X-ray diffractogram of a 4H-SiC substrate coated with Ti at 960°C for 10 minutes with about 35 nm thickness. Aside from the diffraction peaks of the substrate, a set of five other peaks can be observed. These peaks are (000l) diffraction peaks of Ti₃SiC₂ phase, with l = 2, 4, 6, 8 and 10. There are also two small peaks at around 27° and 43° which correspond to (h00) peaks of Ti₅Si₃ with h = 2 and 3. This phase can accommodate considerable amounts of C and thus is usually referred to as Ti₅Si₃C_x.^{23,24} It has hexagonal crystal structure with P6₃/mcm space group in which C atoms sit at 2b positions. For the sake of brevity, we will write Ti₅Si₃ here.

We performed I-V measurements to identify the electric behavior of the samples. A typical plot is

shown in the inset in Figure 1. The linear characteristic of the plot reveals the Ohmic property of the contact. The fact that no post-treatment was done for the samples shows that our method is capable of synthesizing as-deposited Ohmic contacts.

To elucidate the growth mechanism, we first studied the effect of temperature on the growth of Ti_3SiC_2 . For that purpose, we performed two 10-minute Ti depositions on 4H-SiC at 800 and 900°C, for which the X-ray diffractograms are shown in Figures 2 (a) and (b), respectively. In Figure 2(a), only substrate peaks can be seen. TEM studies (not shown) on this sample showed that the film consists of Ti_5Si_3 nanocrystals and of TiC_x , the latter nearly exactly overlaps the substrate diffraction peak. In Figure 2(b), other than the substrate peaks, the rest are those of Ti_3SiC_2 and Ti_5Si_3 . This shows that at 800°C the temperature is not high enough for the growth of Ti_3SiC_2 by Ti deposition on 4H-SiC.

To clarify how the reaction between sputter-deposited Ti and 4H-SiC continues over time, we synthesized samples with different deposition times. Figure 2 (c) shows the XRD pattern of a sample deposited for 30 minutes at 960°C. As can be seen, the plot shows diffraction peaks of Ti_3SiC_2 and Ti_5Si_3 . The small peak at $2\theta \approx 35^\circ$ is the (002) peak of Ti_5Si_3 . Figure 2(d) is the XRD pattern of a sample deposited for 150 minutes, at 960°C. Aside from larger diffraction peaks of Ti_3SiC_2 , the (002) peak of Ti_5Si_3 shows a dramatic increase in intensity. This result suggests that at longer deposition times the growth of Ti_5Si_3 dominates that of Ti_3SiC_2 .

SEM and EDX were used to investigate the surface characteristics of samples synthesized at 960°C with different deposition times of 10, 30, and 150 minutes. Figure 3(a) is an SEM image of the sample deposited for 10 minutes showing the film to be composed of plate-like grains. This is a typical surface morphology of Ti_3SiC_2 .^{17,18} Aside from the plate-like grains, there are also some unevenly distributed faceted islands at the surface, as shown in Figure 3(b). EDX mapping of the C K α 1 peak of the image

shows lower C content in comparison to the rest, Figure 3(c). This result together with the low-intensity X-ray diffraction peak of Ti_5Si_3 in Figure 1 shows that the faceted islands are Ti_5Si_3 phase. Figures 3(d), (e), and (f), which correspond to deposition at 960°C for 10, 30, and 150 minutes, respectively, show how the surface morphology changes with increasing deposition time. A 10-minute deposited sample, (Figure 3(d)), has plate-like grains of Ti_3SiC_2 with few grains of Ti_5Si_3 on top. Continuing the deposition for another 20 minutes, the Ti_5Si_3 grows in size which is illustrated in Figure 3(e). Figure 3(f) shows that 150-minute deposition results in full coverage of the surface with faceted islands of Ti_5Si_3 phase.

Figure 4 (a) shows a low magnification TEM image of the sample deposited at 960°C for 150 minutes. Ti_3SiC_2 and Ti_5Si_3 are two distinct phases in the film. Ti_3SiC_2 is located at the interface of the substrate and the film, while Ti_5Si_3 grows at a higher thickness on top of Ti_3SiC_2 , in agreement with XRD and SEM/EDX results. High resolution TEM images (HRTEM) and corresponding SAED patterns of the two different phases are shown in Figures 4 (b) and (c). These results corroborate the findings from XRD and SEM and show the growth of Ti_3SiC_2 and Ti_5Si_3 .

Based on these results, we can propose a growth mechanism for our experiments. The growth of Ti_3SiC_2 and Ti_5Si_3 can only occur if the 4H-SiC substrate acts as a source of Si and C. Initially, deposited Ti metal grows onto the 4H-SiC surface. For the growth of Ti_3SiC_2 , Si incorporation in TiC_x , which lowers the twinning energy, is a known growth step and requires initial crystallization of TiC_x .^{25,26} In addition, it has been experimentally shown that Ti reacting with SiC initially results in the formation of TiC_x and release of Si, because of the higher affinity of Ti to C than to Si.²⁷ Thus, in our experiments, out-diffusion of C from the substrate into the growing Ti layer and subsequent crystallization of TiC_x is required as the first step of the growth process. These steps can be summarized in the reaction:

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123 In reaction (1), Si can initially remain within a Si-rich region in 4H-SiC. After this step, Si atoms out-
124 diffuse from the substrate into the TiC_x . Si incorporation in TiC_x leads towards the formation of more
125 complex Ti_3SiC_2 structure.²⁷ This subsequently forms the Si planes in the structure of Ti_3SiC_2 in the
126 overall reaction:

127

129

130 Depending on the amount of C in the initial TiC_x phase, the remaining C content from reaction (2), if
131 any, would take part in the subsequent reactions. As the film grows thicker, reactions (1) and (2)
132 require out-diffusion of Si atoms along the Si planes in Ti_3SiC_2 or along boundaries between grains
133 and/or domains which results in an available supply of Si. In addition, the supply of Si would be more
134 than that of C because of prior incorporation of C in TiC_x . Consequently, this results in the growth of
135 Ti_5Si_3 dominating Ti_3SiC_2 and explains the gradual change of the phase at the surface from Ti_3SiC_2 to
136 Ti_5Si_3 . This step is summarized as:

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140 In reaction 3, the C content can be the remnant from reaction 2 or the substrate.

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142 In summary, we have reported a method to synthesize as-deposited Ohmic Ti_3SiC_2 contacts on 4H-SiC,
143 by using direct reaction of sputter-deposited Ti with 4H-SiC substrates. The growth mechanism is

144 based on the surface reaction of sputter-deposited Ti on 4H-SiC. This single-step process provides the
145 possibility for in-situ fabrication of oxygen-barrier capping layers, which are necessary for the use of
146 the contacts in high temperature and corrosive environment.

147

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Figure captions:

Figure 1 X-ray diffractogram of a 4H-SiC substrate coated with Ti at 960°C for 10 minutes, inset: I-V curve.

Figure 2 X-ray diffractograms of samples deposited at (a) 800°C and (b) 900°C for 10 minutes, and of samples deposited at 960°C for (c) 30 minutes, and (d) 150 minutes.

Figure 3 SEM images and EDX mapping of 4H-SiC substrates coated with Ti at 960°C, (a) 10-minute deposition, showing plate-like Ti_3SiC_2 grains, (b) 10-minute deposition, showing a faceted Ti_5Si_3 grain, (c) 10-minute deposition, showing the EDX data of C $K\alpha$ peak. Surface morphology of samples deposited for (d) 10 minutes, (e) 30 minutes, and (f) 150 minutes.

Figure 4 (a) Low resolution TEM image of a 4H-SiC coated with Ti at 960°C for 150 minutes, HRTEM image and SAED pattern along the $[1-100]$ zone axis of (b) Ti_3SiC_2 , and (c) Ti_5Si_3 .

Figure 1

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Figure 2

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Figure 3

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Figure 4
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