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Parametric investigation of the formation of epitaxial Ti_3SiC_2 on 4H-SiC from Al-Ti annealing

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ABSTRACT

The growth of Ti_3SiC_2 thin films was studied onto 4H-SiC (0 0 0 1) 8° and 4°-off substrates by thermal annealing of Ti_xAl_{1-x} ($0.5 \leq x \leq 1$) layers. The annealing time was fixed at 10 min under Argon atmosphere. The synthesis conditions were also investigated according to the annealing temperature (900–1200 °C) after deposition. X-Ray Diffraction (XRD) and Transmission Electron Microscope (TEM) show that the layer of Ti_3SiC_2 is epitaxially grown on the 4H-SiC substrate. In addition the interface looks sharp and smooth with evidence of interfacial ordering. Moreover, during the annealing procedure, the formation of unwanted aluminum oxide was detected by using X-Ray Photoelectron Spectroscopy (XPS); this layer can be removed by using a specific annealing procedure.

1. Introduction

The effects of temperature on materials and devices have been of great interest throughout the history of semiconductor research. The aim has been to investigate the high temperature limits of materials and to enhance high temperature semiconductor device performance. Consistent with the relative status of crystal growth technology, SiC high-temperature contacts have generally demonstrated more advanced high-temperature capability than the other Wide Band Gap contacts [1]. The high-temperature functionality of SiC devices is useless without ohmic contacts that are also capable of operation under the same conditions [1,2]. The durability and reliability of metal–semiconductor contacts are the main factor limiting the operational high-temperature limits of SiC electronic devices. Contact metallization at higher temperature than 300 °C presents fundamental reliability challenges that must be overcome [3–6].

Therefore, substantial challenges remain to be overcome before SiC contacts are ready to support prolonged (tens of years) operation in air or in different atmospheres (Nitrogen, vacuum), at ambient temperature up to 600 °C [7,8], so the main objective of this paper is to propose original contacts that can respond to this broad range of requirements.

The number of materials or metals which can allow reaching our objective is rather limited due to the high constraints. In our opinion, the best choice could be to use MAX phases [9–11] (also termed in some publications "metallic ceramics" [12]) since such materials possess a useful combination of both metallic and ceramic characteristics. The Metallic properties are typically characterized by being thermally and electrically conductive; and the ceramics properties are generally characterized by high elastic modulus, and good oxidation and corrosion resistance.

The $M_{n-1}AX_n$, phases ($n = 1, 2$ or 3) are a class of nano-laminated ternary nitrides and carbides, including about 60 know phases [13]. The Titanium Silicon Carbide (Ti_3SiC_2) is one of the best candidate materials because it combines the best properties of metal and ceramics. Moreover, Ti_3SiC_2 shows good properties like high thermal and electrical conductivities around 37 W/m K and $4.6 \times 10^6\ \Omega^{-1}\ m^{-1}$, respectively. Its thermal expansion coefficient, 8×10^{-6}/°C, is also closed to the one of SiC, 4×10^{-6}/°C. It also presents good chemical and physical stability up to 1400 °C [14]. No

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reaction between Ti_3SiC_2 and SiC is known to occur up to 1200 °C or even above so that the interface should remain thermally stable [15]. After reviewing the major properties of the Ti_3SiC_2/SiC stacking, it is obvious that their electronic properties should be further explored.

A survey of the literature shows that the synthesis of MAX phase material has preferentially been conducted by bulk synthesis techniques at temperatures in the region of 1400 °C. In general manner, the elaboration of Ti_3SiC_2 is difficult; in particular it is challenging to synthetize thin films of Ti_3SiC_2 with a good stoichiometric by using RCVD and CVD [16,17] or magnetron sputtering [18–23]. Epitaxial growth of Ti_3SiC_2 on 4H-SiC, on-axis and misoriented, by annealing of Al-Ti layered structures was already reported [24–29]. However, the chemical paths leading to the formation of single phase were not well understood and many questions remain still unanswered. Mechanism of segregation of Al and Si excesses and the possible formation of amorphous oxides is still under debate.

The goal of this study is to investigate the formation of Ti_3SiC_2 on 4H-SiC(0 0 0 1) 8°- and 4°- off after annealing Ti-Al based stacking, particular attention is given on the influence of the composition and the annealing parameters.

2. Experimental

The samples used for this study were n-type $(0\,0\,0\,1)_{Si}$ 8° and 4°-off misoriented 4H-SiC substrates. Before metal deposition, the samples were chemically cleaned to remove any surface pollution. This includes different solution baths: Trichloroethylene, acetone and ethanol ultrasonic degreasing for 5 min each, followed by two times H_2SO_4: H_2O_2 (75: 25) for 10 min and finally dipped in HF acid diluted at 5% for 4 min, before rinsing with deionized water. After cleaning, 2 types of deposition were carried on the substrates:

(1) 200 nm of Ti_xAl_{100-x} was deposited onto SiC substrates by magnetron sputtering from Ti_xAl_{100-x} targets (where x = 20, 30, 50 at.%) in a high vacuum system. The deposition was carried out at room temperature under an Ar constant pressure (5×10^{-3} mbars).
(2) 200 nm of pure Ti was deposited by using an e-beam evaporator in a high vacuum chamber using high purity titanium.

The samples were then annealed at 900, 1000, 1100 and 1200 °C respectively for 10 min under Ar atmosphere in a rapid thermal annealing (RTA) furnace (heating rate of about 20 °C/s).

The structural investigations were mainly performed by using x-ray diffraction (XRD), and transmission electron microscopy (TEM). The elementary qualification and profiling were done by X-Ray photoelectron spectroscopy (XPS). The XRD measurements were performed with a Rigaku Smartlab diffractometer having monochromatized Cu Kα radiation. The TEM analysis was performed at Pprime Institute. Cross-sectional TEM (XTEM) samples were thinned down to 10 μm by using the tripod polisher. The electron transparency was achieved by ion milling. Conventional and high-resolution transmission electron microscopy (HRTEM) observations were carried out using a JEOL 2200FS microscope (Schottky-FEG, 200 kV) fitted with an omega filter.

The XPS measurements were carried out using PHI Quantera SXM instrument (Physical Electronics, Chanhassen, USA) equipped with a 180° hemispherical electron energy analyzer and a monochromatized AlK_α (1486.6 eV) source operating at 5 kV and 4 mA. The pass energy selected for all elements in profiling mode was 140 eV (corresponding to a spectral resolution of 0.95 eV on

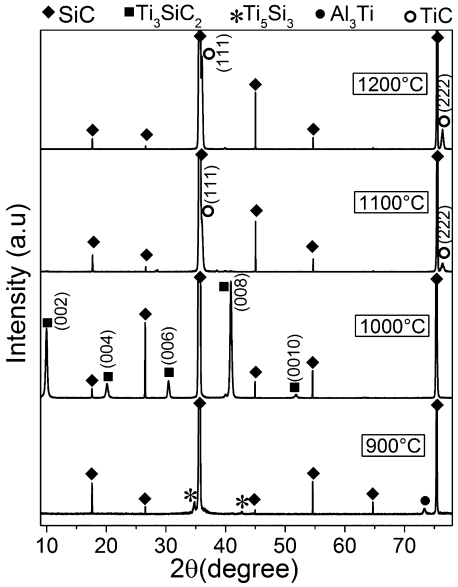

Fig. 1. XRD θ–2θ scan of $Ti_{30}Al_{70}$ after annealing at 900, 1000, 1100, 1200 °C during 10 min under Ar atmosphere.

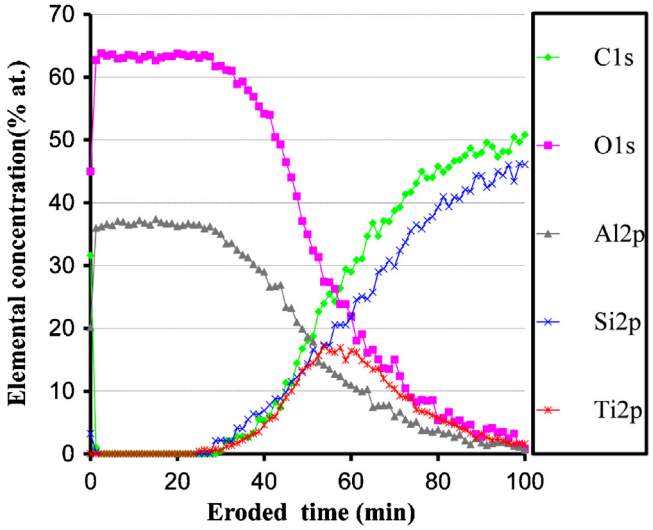

Fig. 2. XPS depth profile of C, O, Al, Si and Ti of the $Ti_{30}Al_{70}$ onto 4H-SiC annealed at 1000 °C for 10 min.

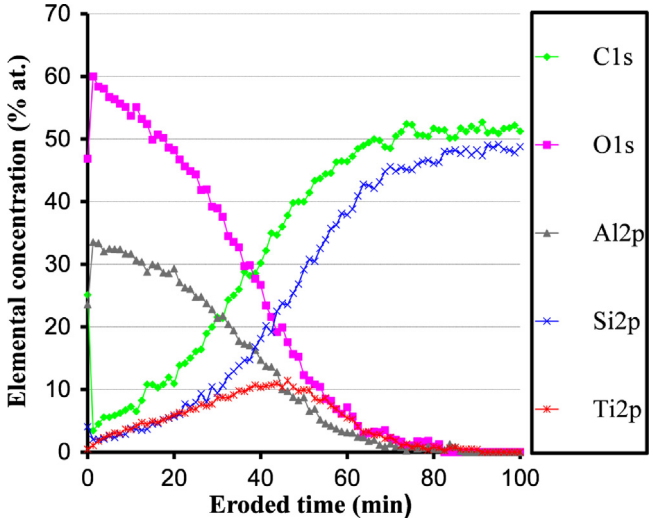

Fig. 3. XPS depth profile of C, O, Al, Si and Ti of the $Ti_{30}Al_{70}$ onto 4H-SiC annealed at 1100 °C for 10 min.