Materials Science and Engineering B 191 (2015) 57–65

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

# Effects of annealing temperature on the structure and electrical properties of tungsten contacts to n-type silicon carbide

Jacek Rogowski [a,*], Andrzej Kubiak [b]

[a] Institute of General and Ecological Chemistry, Technical University of Lodz, ul. Zeromskiego 116, 90-924 Lodz, Poland
[b] Department of Semiconductor and Optoelectronic Devices, Technical University of Lodz, ul. Wolczanska 211/215, 90-924 Lodz, Poland

ARTICLE INFO

*Article history:*
Received 24 June 2014
Received in revised form 22 October 2014
Accepted 29 October 2014
Available online 8 November 2014

*Keywords:*
Ohmic contact
SiC
Tungsten
TOF-SIMS
Specific contact resistance

ABSTRACT

Tungsten contacts deposited on n-type 4H-SiC substrates were annealed at temperatures from 700 to 1400 °C and the phase composition of the contact layers was analyzed by TOF-SIMS technique, X-ray diffraction method and scanning electron microscopy. $W_5Si_3$ and WC were characterized as the main crystalline phases formed in the contact layer after annealing at 1400 °C and crystallite size was calculated as equal to 74 nm and 73 nm, respectively. Measurements of current–voltage characteristics showed that ohmic character of the contact was obtained after annealing at the highest applied temperature 1400 °C while *I–V* characteristics of 1200 °C annealed contact showed limited deviation from linearity. The specific contact resistivities equal to $2.42 \times 10^{-5}\ \Omega\,cm^2$ and $2.27 \times 10^{-5}\ \Omega\,cm^2$ were achieved for 1200 and 1400 °C annealed contacts, respectively. The mechanism of ohmic contact formation was proposed.



## 1. Introduction

Silicon carbide is an object of great interest in the prospective of its application as a material for production of thermally resistant, high power electronic devices capable of operating at a temperature as high as 600 °C [1,2]. Moreover, SiC is characterized by high electron mobility and large saturated drift velocity, which makes it an appropriate material for the production of high frequency semiconductor devices [3,4]. In order to fully exploit the unique properties of SiC for fabrication of electronic devices, reliable metal contacts of low resistivity, which additionally shows both physical and chemical stability at elevated temperatures, should be developed. The process of ohmic contact formation demands the deposition of an appropriate metal on the semiconductor surface. However, such as-deposited structures usually show rectifying *I–V* characteristics, therefore an additional step of contact processing is necessary to obtain an ohmic character of the contact. There are two main techniques to obtain the ohmic character of the contacts. One technique comprises generation of a high carrier concentration in SiC by ion implantation in order to decrease the width of the Schottky barrier. The drawback of this method is the formation of lattice defects during ion irradiation [5]. In order to remove generated defects and to activate implanted atoms, annealing of the SiC sample is needed at temperatures as high as 2000 °C. Such high temperature processing is of limited application because the surface of SiC degrades at temperatures above 1300 °C in argon atmosphere or in vacuum. The other method of ohmic contact formation is the annealing of the as-deposited contact at an appropriately high temperature [6,7]. Since the annealing of the contact leads to the interaction between metal and silicon carbide, it is conceivable that electrical properties of the contact after annealing will be determined by metal–SiC interface, particularly by the properties of the new phases formed in the interface region as a result of the reaction between metal and SiC. In this context analysis of the structure and the chemical composition of the contact interface after annealing is important to clarify the mechanism of the ohmic contact formation.

Among a variety of metals, nickel is one of the most frequently used material for the ohmic contact formation to n-type SiC. Although at present Ni/SiC ohmic contacts of satisfactorily low resistivity in the range $10^{-6}$–$10^{-7}\ \Omega\,cm^2$ [8] can be obtained, they are prone to degradation during prolonged work at an elevated temperature. It was suggested that graphite phases, which are formed as a result of a thermally induced reaction between Ni and SiC during the annealing of the Ni/SiC structure, can be responsible for their thermal instability [9,10]. Moreover, carbon layer deposition on the surface of Ni/SiC after annealing can pose a problem with the mounting of the wire [11].

In order to avoid an undesirable influence of graphite on thermal stability of metal/SiC ohmic contacts, metals such as Cr, Fe, Ti and W,

* Corresponding author. Tel.: +48 426313099.
*E-mail addresses:* jacek.rogowski@p.lodz.pl (J. Rogowski), andrzej.kubiak@p.lodz.pl (A. Kubiak).

http://dx.doi.org/10.1016/j.mseb.2014.10.015

which react with SiC to give both silicides and stable carbides, are of interest as contact material [12]. Among these metals tungsten is of special interest because of it is refractory properties and the fact that it is already used in Si based device technology [13]. Tungsten reactivity toward SiC has been a subject of several studies. Experimental studies showed that the onset of the reaction between the deposited W and SiC varies upon the metal deposition method [13–17]. Seng and Barnes calculated the ternary phase diagrams of W–Si–C system in the temperature range from 300 to 2200 K [18]. Calculation results showed that the products of the reaction between W and SiC depend on the temperature of the reaction and both tungsten carbides and tungsten silicides are present in the most stable systems. Additionally, for bulk tungsten–SiC system phase sequence in contact interface was explained using ternary phase diagrams [13]. The formation of Ohmic W contacts to SiC was reported in the literature [13,15,19,20]. Specific contact resistivity (SCR) in the range 0.17–0.27 $\Omega\,cm^2$ was obtained after annealing the W/SiC structure at 1000 °C. However, annealing at higher temperatures led to the increase in SCR accompanied by deterioration of the surface quality together with WC phase precipitation [13]. Lower specific contact resistivity ($2 \times 10^{-3}$–$7 \times 10^{-4}\,\Omega\,cm^2$) of W contacts to 6H-SiC was also obtained but the description of contact processing was not given [19].

Tungsten was also used as a contact material in combination with other metals like nickel or titanium. Formation of titanium–tungsten ohmic contact with specific contact resistance of $3.3 \times 10^{-5}\,\Omega\,cm^2$ to n-type 4H-SiC epilayer with doping concentration of $1.1 \times 10^{19}\,cm^{-3}$ were reported [21]. A high thermal stability was observed for W–Ni ohmic contacts to n-type 4H-SiC characterized by specific contact resistivity of $7.69 \times 10^{-4}$ and $5.81 \times 10^{-4}\,\Omega\,cm^2$ for doping level equal 1.4 and $2 \times 10^{19}\,cm^{-3}$, respectively [22]. Similar value of specific contact resistivity equal $5 \times 10^{-4}\,\Omega\,cm^2$ was obtained for W–Ni ohmic contact to n-type epitaxial layer with doping concentration in the range 5–$7 \times 10^{18}\,cm^{-3}$ deposited on p-type 4H-SiC substrate [23].

The aim of this study was to investigate the dependence of electrical properties of the tungsten contacts to SiC on the structure and chemical composition of their interface region. As thermal processing is required to obtain the ohmic character of the W/SiC contacts, some changes of chemical composition of the contact interface must occur during annealing. TOF-SIMS along with XRD method were used to investigate the spatial distribution of the new phases formed as a product of the reaction between tungsten and SiC during annealing in order to find factors responsible for the ohmic character of W/SiC contact.

## 2. Experimental

Nitrogen doped n-type 4H-SiC polytype wafer, Si-face polished and with resistivity $\leq$0.025 $\Omega$ cm purchased from SiCrystal AG was used as a substrate material. SiC samples were 7 mm × 7 mm squares cut from 2 inch wafers.

Before the metallization fabrication a cleaning process was performed using sequentially $H_2O$:$NH_4OH$:$H_2O_2$ (5:1:1) mixture at 80 °C for 10 min to remove organic contamination, $H_2O$:HCl:$H_2O_2$ (6:1:1) mixture at 80 °C for 10 min to remove metal impurities and HF (40%) for surface oxide removal. Each step was followed by rinsing in deionized water for 1 min. After chemical cleaning, the samples were blown dried by nitrogen and oxygen plasma etching of the sample surface was applied for 30 min.

Tungsten contacts were prepared on the polished, Si faced side of SiC substrates. Magnetron sputtering was used for deposition of tungsten (99.995% purity, Kurt J. Lesker). The thickness of the metal layer was 400 nm. After metallization the samples were annealed in Ar atmosphere for 10 min at different temperatures (700, 800, 900, 1000, 1200 and 1400 °C).

Circular transfer length method (CTLM) and current–voltage (*I–V*) characteristics were used to evaluate the specific contact resistance. CTLM technique is commonly used for measurements of resistivity of the metal contacts on the semiconductor substrate [24]. Two sets of CTLM structures with a different inner contact diameter (200 μm and 500 μm) were prepared for electrical measurements. Each of these sets consisted of eight structures with a distance between the inner and outer region from 10 μm to 80 μm.

X-ray diffraction (XRD) analyses were carried out in order to identify the formed phases and their crystallographic orientation. The analyses were performed using a XPERT PRO MPD diffractometer with a Cu $K_\alpha$ anode in the Bragg–Brentano arrangement.

TOF-SIMS IV secondary ion mass spectometer (ION-TOF, Münster, Germany) was used for analysis. It is equipped with a time of flight analyzer of a reflectron type and bizmuth primary ion gun working at 25 kV. $Bi_3^+$ primary ions were used in this analysis. Average primary ion current was 0.6 pA. Sample sputtering was performed using additional ion gun provided with separate $O_2^+$ and $Cs^+$ ion sources. For TOF-SIMS profiles of positive secondary ion emission analysis 3 keV $O_2^+$ ion beam was used for sputtering of the sample material. Current intensity of $O_2^+$ ion beam was set to 100 nA. In the case of negative secondary ion emission analysis 3 keV $Cs^+$ ions were used and current intensity was 34 nA. During the TOF-SIMS analysis samples were at room temperature and at the pressure of $5 \times 10^{-9}$ mbar. TOF-SIMS images were recorded using the burst alignment mode of the $Bi^+$ primary ion gun operation. The TOF-SIMS images of the contact interface presented in Fig. 7 were collected using $Bi^+$ primary ions in the high current bunched mode of primary ion gun operation.

Scanning electron microscope (Hitachi S-4700, Japan) equipped with an energy dispersive X-ray spectrometer (EDS, Thermo NORAN, USA) was used for the contact surface analysis.

## 3. Results

### 3.1. Electrical characterization

The *I–V* characteristics of the W/SiC contacts before and after annealing in Ar at selected temperatures in the range 700–1400 °C are shown in Fig. 1. The Schottky character was observed for the as-deposited and annealed contacts for the temperatures up to 1200 °C. Although annealing at 1200 °C caused the *I–V* characteristics of contact to shift toward the ohmic behavior, the fully ohmic

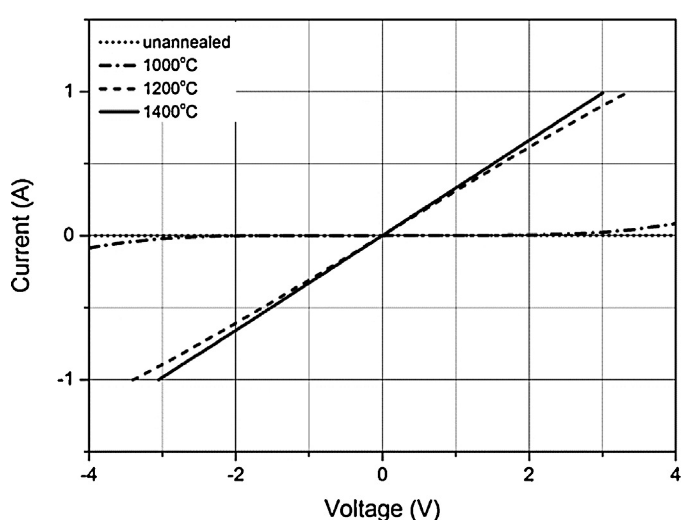


**Fig. 1.** Current–voltage characteristics of W contact to n-type 4H-SiC before and after annealing at 1000 °C, 1200 °C and 1400 °C.