Comparison of nickel, cobalt, palladium, and tungsten Schottky contacts on n-4*H*-silicon carbide

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Abstract

We have investigated the current-voltage (*I-V*) characteristics of nickel (Ni), cobalt (Co), tungsten (W) and palladium (Pd) Schottky contacts on n-type 4*H*-SiC in the 300-800 K temperature range. Results extracted from *I-V* measurements of Schottky barrier diodes showed that barrier height (Φ_{Bo}) and ideality factor (n) were strongly dependent on temperature. Schottky barrier heights for contacts of all the metals showed an increase with temperature between 300 K and 800 K. This was attributed to barrier inhomogeneities at the interface between the metal and the semiconductor, which resulted in a distribution of barrier heights at the interface. Ideality factors of Ni, Co and Pd decreased from 1.6 to 1.0 and for W the ideality factor decreased from 1.1 to 1.0 when the temperature was increased from 300 K to 800 K respectively. The device parameters were compared to assess advantages and disadvantages of the metals for envisaged applications.

Key words: Silicon carbide, Metal-semiconductor, Schottky contacts, silicide, barrier height, ideality factor.

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1. Introduction

In modern society, there is a growing demand for electricity and on the other hand we are trying to save energy in order to reduce carbon dioxide emissions into the atmosphere. This scenario has forced us to design more efficient power electronic devices. Silicon carbide (SiC) is considered as the semiconductor material that will empower us to move from traditional silicon power electronics into smart power. This is because silicon (Si) power components have almost reached their maximum performance capability, hence there is need to find alternative semiconductor materials, such as SiC or gallium nitride (GaN), to improve semiconductor device performance.

SiC is a compound semiconductor material which has better electrical properties compared to Si; with approximately three times greater band gap, ten times higher dielectric breakdown and three times larger thermal coefficient. These electrical characteristics make it an ideal candidate for power electronics applications [1, 2]. It has attracted research and commercial interest on electrical device applications due to the increase in availability of high quality wafers and improvement in material fabrication techniques [3]. The material is preferable for device applications due to good electron mobility and the high isotropic nature of many of its electrical characteristics [4]. In addition, its large band gap makes it useful for the design of devices with low series resistance and low power dissipation [5]. 4*H*-SiC is one of its many polytypes. The properties and applications of Schottky barrier diodes (SBDs) fabricated on 4*H*-SiC are not thoroughly understood despite the fact that they have been available on the market for a long time [6]. Of particular research interest is to add more knowledge to the processing steps involved in the fabrication of 4*H*-SiC devices and establish consistent control of metal contact properties on semiconductors

[7-9]. In order to obtain ideal rectifying contacts high Schottky barriers are required [10].

In this study, the electrical characteristics of four different metal-4*H*-SiC systems were investigated and compared by fabrication of SBDs and characterizing them. These metals were Pd, Ni, W and Co with work functions of 5.22, 5.01, 5.00 and 4.03 eV respectively [11]. According to the ideal diode theory the Schottky barrier height of a metal semiconductor interface is simply the difference between the metal work function and the electron affinity of the semiconductor [12]. This means that a metal with a higher work function will produce a higher Schottky barrier. The role of the metal work function has however been downplayed by other researchers who have a viewpoint that the Schottky barrier is not homogeneous [13]. These include Gammon et al [14] who have accurately modeled, parameterized and fitted *I-V-T* characteristics on Ni/4*H*-SiC incorporating interface effects of an inhomogeneous barrier. The choice of metals was also based on their high melting points of 1554 °C, 1453°C, 1495 °C and 3140 °C for Pd, Ni, Co and W respectively. 4*H*-SiC has high potential for use in high temperature applications. The metals have all in the past been successfully used to fabricate devices on 4*H*-SiC. An example is W which has been approved for fast switching, high voltage and high temperature applications on 4*H*-SiC [15].

In past studies on metal/4*H*-SiC device structures, current-voltage-temperature (*I-V-T*) characteristics of SBDs using ideal thermionic emission theory have revealed behaviors that contradict semiconductor theory such as increase in barrier height with increasing temperature [16, 17]. Because of a semiconductor`s negative temperature coefficient, the barrier height is expected to be higher at lower temperatures, as at such temperatures the electrons will have less energy to surmount the barrier. These

deviations have been assumed to be caused by the presence of inhomogeneities at the metal-semiconductor junction which have been speculated to be due to doping concentration irregularities, high interface state densities, surface defects and reactions at the metal-semiconductor interface [18-20].

Previous studies on metal-SiC systems have shown metals to be thermodynamically unstable on SiC, undergoing interfacial reactions with the semiconductor following phase diagrams but in accordance with different morphologies [21-24]. In a comparative study of metals on 6*H*-SiC, Goesman et al [23] showed that different metals have their own advantages and disadvantages. For example, Ni had a high contact resistance whilst W did not adhere well to the semiconductor. Most of the past investigations were focused on the production of ohmic contacts therefore a metal deposition was followed by a rapid thermal annealing to form a silicide [25]. In some cases techniques used did not optimize the electronic properties of the metal-SiC interface by technological measures, for example contact being attained by pressurizing W foil [21].

The scope of this work was to compare these metals and find one which is most ideal for use as a contact for various electronics applications. An ideal metal contact would give high barrier heights and low series resistances. Accurate, non-destructive, and easy-to-use electrical characterization techniques were used, so that vital parameters such as, series resistance (R_s), reverse leakage current (I_R), Schottky barrier height (Φ_{Bo}), and ideality factor (n) were determined, in order to assess the material quality and device reliability. Sound device fabrication protocols were followed and *I-V* characteristics of Ni/, Co/, W/ and Pd/n-4*H*-SiC SBDs were measured. The data was analyzed using thermionic emission theory to yield important information on Schottky diode parameters and their temperature dependence in the 300 - 800 K temperature

range. We also investigated whether there was a correlation between reported metallurgical reactions at the metal-semiconductor interface and our observed electronic aspects. Understanding contact properties is important for eventual better device control [26].

2. Experimental procedure

We used n-type 4*H*-SiC wafers doped with nitrogen supplied by Cree Inc. The wafers consisted of an epi-layer of doping density 7×10^{15} cm^{-3} grown on a 4*H*-SiC substrate with a doping density of 10^{18} cm^{-3}. Four samples of the wafers were cleaned in a two-step procedure. The wafers were first degreased by boiling consecutively in three different organic solvents namely tri-chloroethylene, acetone and methanol. They were then washed in deionized water with a resistivity of 18.2 MΩ cm. Thereafter, they were etched by dipping in 2% hydrofluoric acid solution for 60 seconds, followed by a deionized water rinse and dried using nitrogen gas.

Immediately after cleaning, the samples were rapidly transferred into an Edwards Auto 306 vacuum deposition system. The ohmic contact was formed by resistively depositing 3000 Å of Ni on the sample backside followed by heating at 1223 K for 10 minutes in Ar gas. Such a thickness was to minimise the corrosive effect of hydrofluoric acid in subsequent etching steps. Annealing for 10 minutes allows for the formation of Ni silicides which is desirable for a high quality ohmic contact on 4*H*-SiC [25].

After annealing, the degreasing procedure described above was repeated but instead of boiling, samples were placed in an ultrasonic bath at room temperature. Pd, Ni, and Co Schottky contacts were then deposited by vacuum resistive evaporation and the W Schottky contacts were deposited by electron beam deposition.

The vacuum pressure was maintained at approximately 1.0×10^{-6} mbar during the depositions. A mechanical mask was used, through which the metals for Schottky contacts were deposited, resulting in an array of 0.6 mm diameter contacts at a thickness of 500 Å Pd, 1000 Å Ni, 1200 Å Co and 300 Å W on different samples.

After contact fabrication, *I-V* measurements were performed using an HP 4140B pA meter /DC voltage source. Diode parameters such as Φ_{Bo}, R_s, n and I_R were extracted. Temperature dependent *I-V* measurements were carried out at 25 K intervals in the temperature range 300 K-800 K in a JANIS closed cycle liquid helium cryostat.

3. Results and Discussion

According to thermionic emission theory, the *I-V* relationship across a Schottky barrier for ($V > 3kT/q$) is given by [27].

$$I(V) = \underbrace{AA^*T^2 \exp\left(\frac{-q\phi_{Bo}}{kT}\right)}_{I_s}\left[\exp\left(\frac{qV - IR_s}{nkT}\right) - 1\right] \quad (1)$$

where A is the diode area, A^* is the effective Richardson constant (146 A cm^{-2}K^{-2} for n-4H-SiC), V is bias voltage, R_s is the series resistance, n is ideality factor, Φ_{Bo} is the barrier height. I_s is the saturation current which is the intercept of an ln I versus V curve given by the prefactor of the first exponential in Equation 1 [28]. The Φ_{Bo} is calculated from the saturation current as [29]

$$\phi_{Bo} = \frac{kT}{q}\ln\left(\frac{AA^*T^2}{I_s}\right) \quad (2)$$

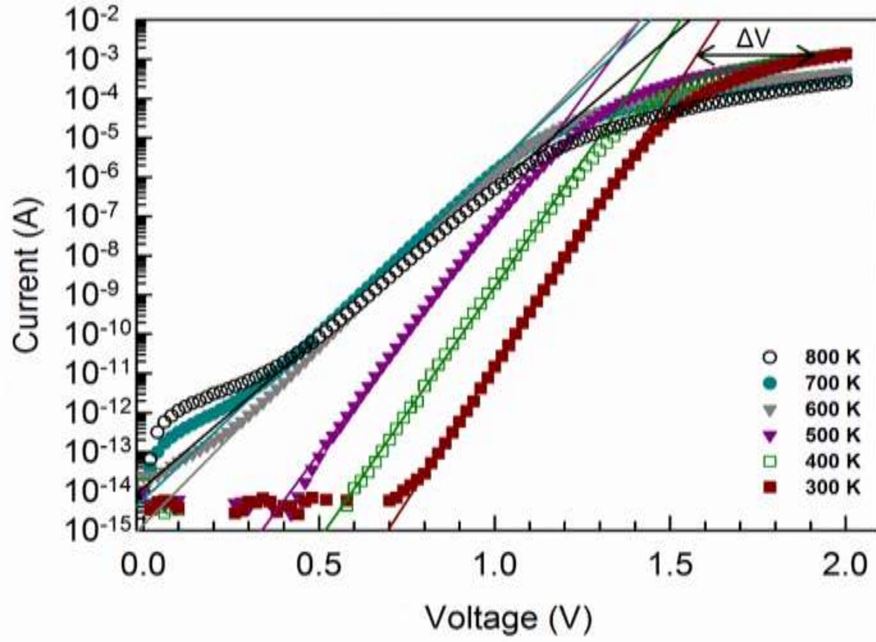

Fig 1 Semi-logarithmic forward bias *I-V* curves as a function of temperature for Pd/n-4H-SiC Schottky barrier diodes.

Figure 1 shows part of the semi-log *I-V* characteristics obtained in the 300-800 K temperature range for the Pd/n-4*H*-SiC SBDs. Similar curves were obtained from the devices fabricated using Co, W and Ni. The curves have linear regions in the intermediate bias regions where least squares fits of Equation 1 were performed as shown in Figure 1. *n* was determined from the slope of these fits as [30].

$$n = \frac{q}{kT}\left(\frac{dV}{d\ln I}\right) \tag{3}$$

From the diagram, *I-V* plots shift towards high bias voltage with decreasing temperature as predicted by Equation 1. Table 1 gives a summary of the parameters obtained from Figure 1.

Table 1: Summary of the temperature dependent values of the Schottky barrier height (Φ_{Bo}), ideality factor (n), series resistance (R_s) and reverse leakage current (I_R) at -1 V obtained from the *I*-*V* characteristics.

Palladium

T(K)	SBH (eV)	n	R_s (Ω)	I_R (A)
300	1.42	1.62	42	8.0×10^{-15}
400	1.47	1.44	32	3.2×10^{-14}
500	1.62	1.28	25	5.9×10^{-13}
600	1.82	1.20	19	8.5×10^{-11}
700	2.11	1.15	18	2.8×10^{-9}
800	2.27	1.20	21	1.8×10^{-8}
Nickel				
300	1.24	1.61	34	1.6×10^{-14}
400	1.40	1.47	27	1.3×10^{-14}
500	1.59	1.29	18	4.1×10^{-13}
600	1.70	1.16	12	4.1×10^{-11}
700	1.83	1.08	12	2.1×10^{-9}
800	1.96	1.01	14	2.0×10^{-8}
Cobalt				
300	1.15	1.59	27	5.5×10^{-14}
400	1.32	1.39	16	1.4×10^{-13}
500	1.46	1.30	8	5.4×10^{-12}
600	1.64	1.18	7	1.8×10^{-10}
700	1.76	1.12	7	4.9×10^{-9}
800	1.92	1.03	8	6.2×10^{-8}
Tungsten				
300	1.26	1.15	53	3.0×10^{-14}
400	1.37	1.05	46	4.6×10^{-13}
500	1.53	1.02	36	3.0×10^{-11}
600	1.62	1.01	29	1.9×10^{-9}

700	1.64	1.00	27	1.3×10^{-7}
800	1.58	1.00	30	8.1×10^{-6}

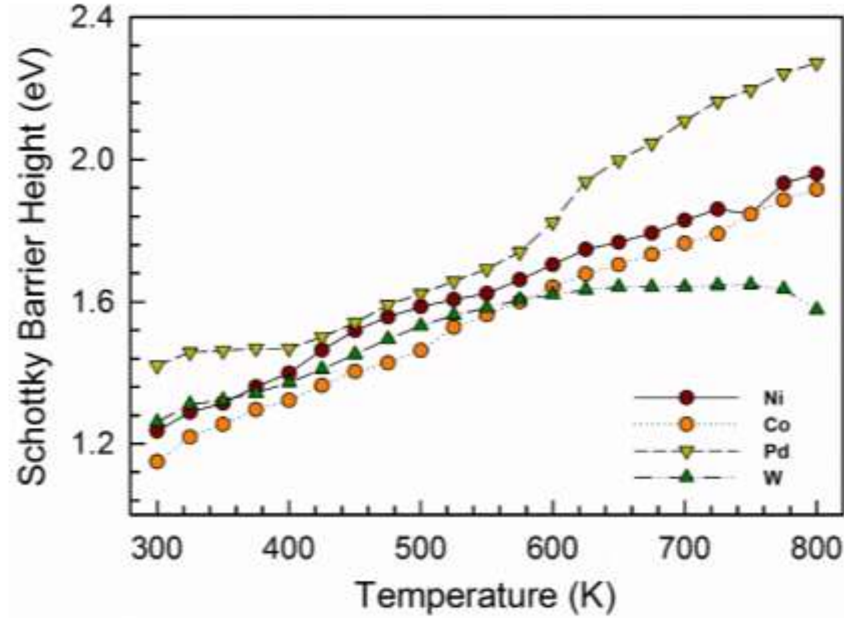

Fig. 2 Schottky barrier height (Φ_{Bo}) against absolute temperature for Ni, Co, Pd and W Schottky contacts on 4*H*-SiC.

The Φ_{Bo} for all the Schottky contacts shows an increase with temperature, e.g. for Pd, it varies from 1.4 eV to 2.3 eV for the temperatures 300 K to 800 K, respectively, as depicted in Figure 2. This trend of increase in Φ_{Bo} with temperature contradicts the negative temperature coefficient and the forbidden gap of semiconductors [27]. Tung explained this using barrier height inhomogeneities as due to nanometer size patches of barrier height set in a uniform high barrier background [13]. From Figure 2 Pd/4*H*-SiC devices give the highest Φ_{Bo} at all temperatures. The barrier height is an important parameter in the operation of devices e.g for enhancement type metal semiconductor field effect transistors (MESFETs) where high barrier height determines the voltage swing. Ni/4*H*-SiC devices also show an average trend of high Φ_{Bo} when compared to those on Co and W. When comparing the general trend in Figure 2 with the work functions of the metals the data appears to

obey the ideal diode theory. Φ_{Bo} appears to be strongly influenced by the metal work function with a higher work function producing a higher Schottky barrier [12]. The highest increase for Pd devices is observed above 620 K. It has been reported that an exothermic reaction occurs between SiC and Pd in the 673 K- 873 K range [31].

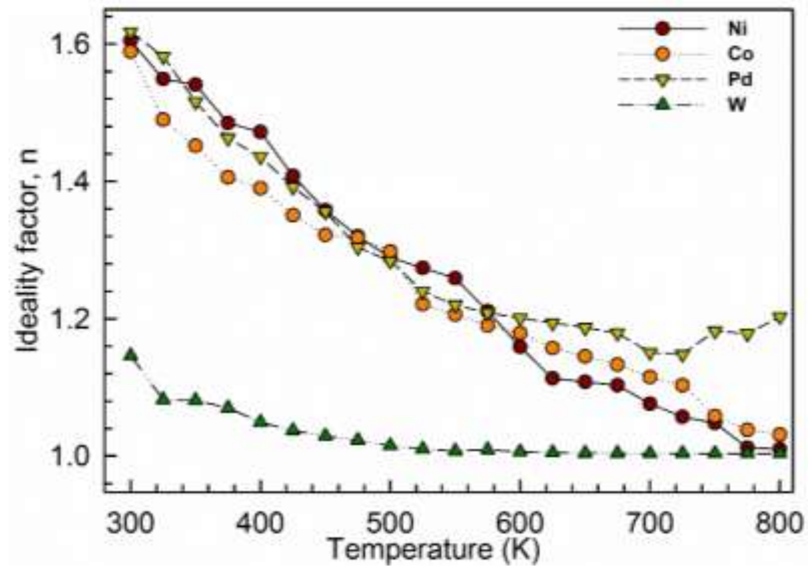

Fig. 3 Ideality factor (n) against absolute temperature for Ni, Co, Pd and W Schottky contacts on 4*H*-SiC.

n generally decreases from 1.6 at 300 K to about 1.0 at 800 K for Ni, Co and Pd as shown in Figure 3. For W, it ranged from 1.15 to 1.0 in the same temperature range. In general Pd and Ni have the highest values whilst W has the lowest. Ideality factor is a measure of adherence to pure thermionic emission theory as it measures barrier deformation under bias [32]. Values of n around 300 K show the presence of other current transport mechanisms across the barrier, such as generation-recombination current, and as the temperature is increased thermionic emission current dominates and hence n closer to unity at 800 K.

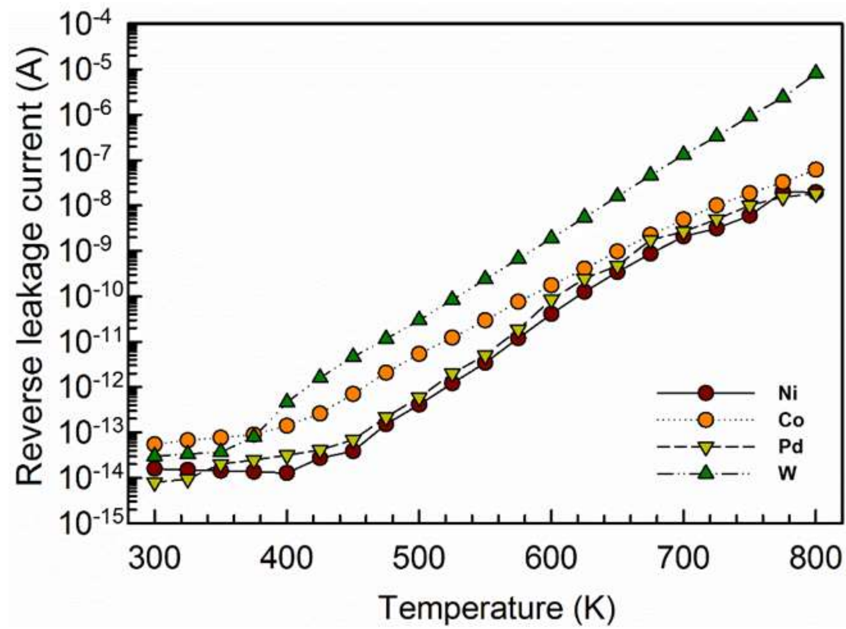

Fig. 4 Reverse leakage current (I_R) measured at -1 V against absolute temperature for Ni, Co, Pd and W Schottky contacts on 4*H*-SiC.

The I_R is the current at reverse bias flowing in the device. It shows whether the device is a good rectifier. A lower value is favourable. This parameter is also important for devices that operate in reverse bias. I_R recorded at a bias of -1 V increased with increasing temperature for all the samples as depicted in Figure 4. For instance, the W devices had ~ 10^{-14} A at 300 K which increased to ~10^{-6} A at 800 K. W devices had on average the highest I_R also showing that they are poor rectifiers and also considering that they had lower barrier heights. The general increase in leakage current with temperature has been attributed to phonon assisted tunnelling of electrons from defect states close to the metal-semiconductor interface in n-GaN [33]. Several electron traps were reported in metal-4*H*-SiC SBDs fabricated by various techniques [34]. Ni devices had the least I_R. Ni and Pd devices had the best rectifying properties.

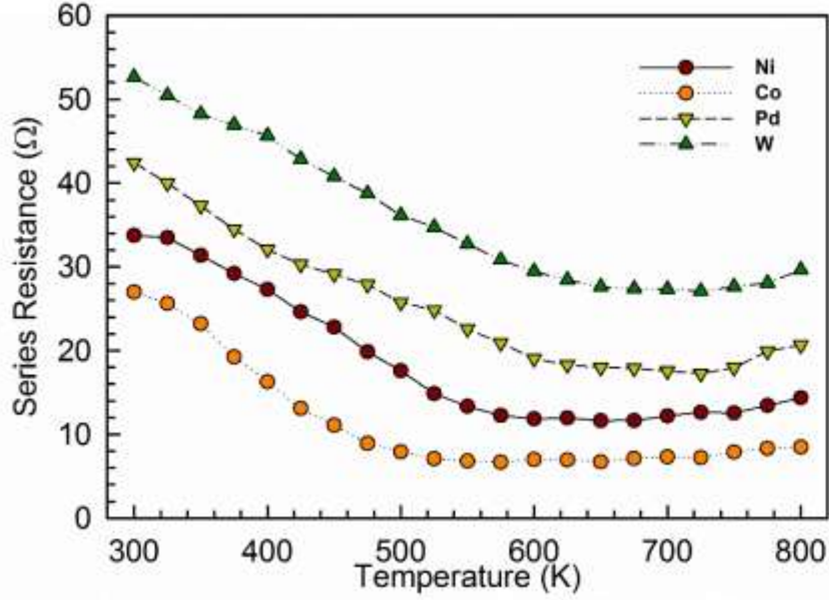

Fig. 5. The plot of series (R_s) resistance against absolute temperature, for Ni, Co, Pd and W Schottky contacts on n-4*H*-SiC

At high voltages on Figure 1, the semi logarithmic *I-V* characteristics deviate from the straight line relationship (linear fit) predicted by the thermionic emission theory (Equation 1). This deviation from the ideal characteristic is due to series resistance. At a given constant current in the high voltage region series resistance is given by the change in voltage measured from a point on the linear fit to a measured point on the *I-V* curve divided by the current as illustrated in Figure 1 by the arrow ΔV which is at 10^{-3} A for the 300 K curve. This series resistance (R_s) is calculated using Ohm`s law according to the equation [12, 21]

$$R_s = \frac{\Delta V}{I} \tag{4}$$

R_s is an undesirable quantity in devices as it results in poor performance and in some cases heating up of devices. R_s for all the contacts discussed is low (< 60 Ω) as exhibited in Figure 4. In fact, there is a steady decrease with increasing temperature from 300 K up to 600 K, e.g. for W having the highest values, R_s decreased from 53 Ω to 30 Ω. Slight increase is observed between 700 K and 800 K for all devices. A similar trend of decrease then gradual increase has been observed by Mayimele et al

in ZnO in the 60 - 300 K temperature range and they attributed it to bulk resistivity and a transition in conductivity [35]. Co contacts had the lowest R_s. This is very desirable in contact fabrication. W contacts had a very high R_s. Nickel contacts also had a relatively low R_s. These results differ from what was observed in reference [23]. This could be attributed to the fact that no optimisation was done to their contact properties. Skipping steps like rinsing off of etchants or inorganic solvents can drastically alter contact properties. R_s became almost constant between 600 K and 800 K. Native defects have been known to contribute to series resistance in other semiconductor materials. 4*H*-SiC contains native defects such as the Z_1Z_2 which has been observed in the temperature region with our measurements. However past studies have de-emphasized the role of these defects in *I-V-T* characteristics of 4*H*-SiC SBDs. Bolen et al found no correlation between defect density and diode parameters [36]. As such we cannot conclude that they contribute to R_s.

4. Conclusions

The *I-V* characteristics of Ni, Co, W and Pd/n-4*H*-SiC Schottky contacts were analysed in the 300-800 K temperature range. Φ_{Bo} and n were found to be strongly dependent on temperature. Φ_{Bo} increased with an increase in temperature a property that contradicts the negative temperature coefficient of semiconductor materials. This trend was attributed to barrier height inhomogeneities. Values of n decreased with an increase in temperature which indicates that thermionic emission current was the dominant transport mechanism at elevated temperatures. There was a general increase of I_R of Ni/-, W/-, Co/- and Pd / n-4*H*-SiC Schottky contacts recorded at -1 V with increasing temperature. Finally, R_s for all the contacts showed an overal decrease with temperature. Pd devices had the most desirable rectification properties with a high

Φ_{Bo} and lower I_R followed by Ni. For applications where R_s has to be critically low, Co devices are the most desirable. W devices appear to have unfavourable parameters but due to the metal`s high melting point, its devices are of choice for extremely high temperature operations.

Acknowledgements

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