Electrical and surface morphological studies of palladium and ruthenium Schottky diodes on *n*-Ge (100)

A. Chawnda[1,2,], F.D. Auret[2], W. Mtangi[2], J.M. Nel[2], M. Diale[2], and C. Nyamhere[3]

[1]Department of Physics, Midlands State University, Gweru, Zimbabwe

[2]Department of Physics, University of Pretoria, 0002, Pretoria, South Africa

[3]Department of Physics, Nelson Mandela Metropolitan University, Box 7700 , Port Elizabeth 6031, South Africa

E-mail: albert.chawanda@up.ac.za

Abstract. Palladium (Pd) and ruthenium (Ru) Schottky barrier diodes were fabricated on (100) Sb-doped *n*-type germanium using resistive evaporation and electron beam deposition systems, respectively. Electrical characterization of these diodes using (*I*-*V*) measurements was performed under various annealing conditions. The morphological evolution of the surface was analysed using the scanning electron microscopy. The variation of the electrical and structural properties of these Schottky diodes can be attributed to combined effects of interfacial reaction and phase transformation during the annealing process. Thermal stability of both the Pd/*n*-Ge (100) and Ru/*n*-Ge (100) Schottky diodes is maintained up to annealing temperature of 550°C. Results have also indicated that the onset temperature for agglomeration in Pd/*n*-Ge (100) system occurs between 500-600°C, and in Ru/*n*-Ge (100) system occurs between 600-700°C.

1. Introduction

As device dimensions are scaled to sub-micrometer dimensions in silicon-based microelectronics, new processes and materials are becoming necessary to overcome the limitations of the conventional methods [1]. Of interest are silicon compatible materials that provide better device performance. Germanium (Ge) is a promising material for high mobility devices due to its higher and more symmetric carrier mobility compared with silicon [2], and its excellent compatibility with high-k materials [3]. The lack of a stable native Ge oxide has been the obstacle for the use of Ge in CMOS devices [4]. However, recent developments of next generation deposited high-k dielectrics, germanium oxynitride, ZrO_2, Al_2O_3 and HfO_2 allow for the fabrication of high performance Ge-based metal-oxide semiconductor field effect transistors (MOSFETs) [5]. Metal germanides may be used as contact materials in future germanium technology. Compared with silicides that have been extensively investigated in the past [6], formation of germanides on single crystal germanium surface attracted less attention. Therefore optimal implementation of germanium technology will require an optimal understanding of metal-germanium interaction from both metallurgical and electronic standpoints. Most of the studies on metal-Ge reaction up to date have been carried out using in-situ annealing by slowly-ramping annealing temperature or rapid thermal annealing processing, rather than using furnace annealing, and also with less emphasis on morphological evolution.

Metal-semiconductor (MS) interfaces are an essential part of virtually all semiconductor electronic devices [7]. The MS structures are important research tools in the characterization of new semiconductor materials [8]. Their interface properties have a dominant influence on the performance, reliability and stability of device [9]. These applications include microwave field effect transistors, radio-frequency detectors, quantum confinement devices and space solar cells [10, 11].

In this study we investigated the change in electrical properties, morphological evolution and microstructure stability of Pd/- and Ru/*n*-Ge (100) Schottky diodes at different furnace annealing temperatures in the temperature range 25-700°C.

2. Experimental procedures

To study the thermal annealing behavior of the Schottky diodes, we have used bulk-grown (100) oriented, *n*-type Ge, doped with antimony (Sb) to a density of 2.5×10^{15} cm^{-3} supplied by Umicore. Berfore metallization the samples were first degreased and the etched in a mixture of H_20_2: H_2O (1:5) for 1 minute. Immediately after cleaning, the samples were inserted into a vacuum chamber where AuSb (0.6% Sb), 100 nm thick, was deposited by resistive evaporation as an ohmic contact. A ten-minute anneal at 350°C in argon (Ar) to lower the barrier height and increase the ohmic behavior of the contact was performed. Before Schottky contact deposition, the samples were again chemically cleaned as described above. Pd Schottky diodes were resistively deposited under vacuum below 10^{-6} Torr, while Ru Schottky diodes were deposited by using an electron beam deposition system. The diodes were (0.60±0.05) mm in diameter and 30 nm thick. The thickness of the diodes and deposition rate were monitored by using an INFICON XTC 751-001-G1 quart crystal thickness monitor. After the diodes fabrication, the samples were characterized by using current-voltage (*I-V*) measurements. The electrical characterization was repeated after every annealing cycle in Ar ambient for 30 minutes between 25°C and 575°C. Characterization of the films for as-deposited and after different annealing temperatures was accomplished using a ZEISS ULTRA PLUS scanning electron microscopy (SEM) system operating at 1 kV.

3. Results

The Schottky barrier heights (SBHs) of the diodes were calculated from *I-V* characteristics, which were analyzed by the thermionic emission (TE) model given by [9,12]:

$$I(V) = I_0 \exp\left(\frac{qV}{nkT}\right)\left[1 - \exp\left(-\frac{qV}{kT}\right)\right] \tag{1}$$

where I_0 is the reverse saturation current given by the following relation [13]:

$$I_0 = AA^* T^2 \exp\left(-\frac{q\Phi_B}{kT}\right), \tag{2}$$

obtained from the straight line intercept of ln I at $V = 0$, A^* is the effective Richardson constant, A is the diode area, T the measurement temperature in Kelvin, k the Boltzmann constant, Φ_B is the zero bias effective Schottky barrier height (SBH), q is the electronic charge and n the ideality factor which can be determined accurately from the slope of the linear part of a ln I versus V plot, assuming pure thermionic emission can be obtained from equation (1) as

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

which is equal to 1.0 for an ideal diode and usually has a value greater than unit.

Figure 1 shows the variation of the SBH and reverse current at -1 V with annealing temperature for Pd Schottky diodes on *n*-Ge (100).

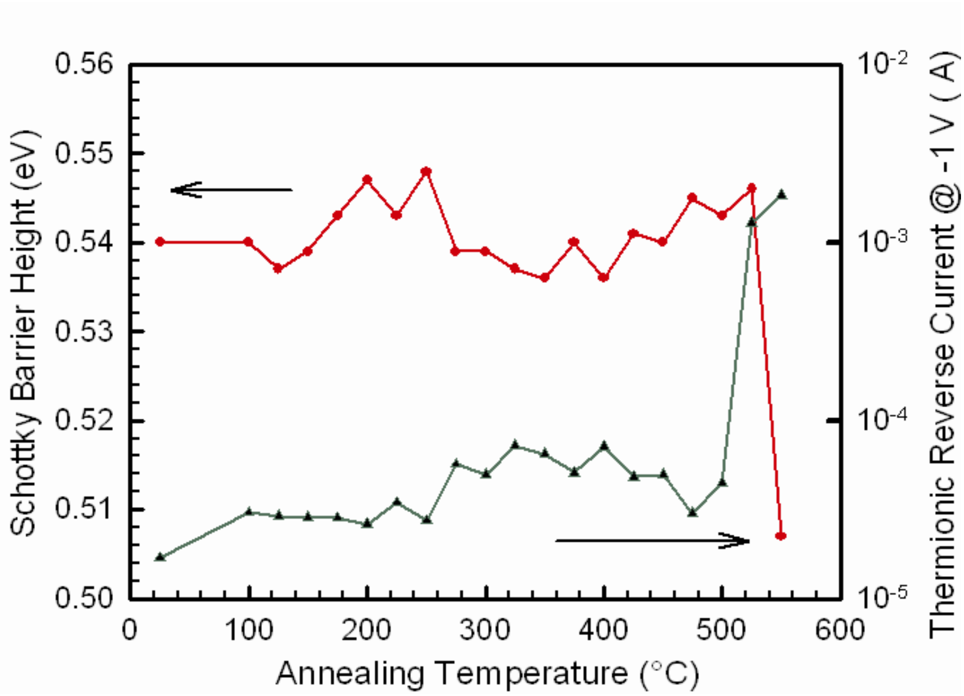


Figure 1. Plot of the Schottky barrier height and reverse current at -1 V as a function of annealing temperature for Pd/n-Ge (100) Schottky diodes.

The SBH and reverse current at a bias voltage of -1 V for as-deposited Pd/*n*-Ge (100) Schottky diodes were found to be (0.540 ± 0.005) eV and (17.00 ± 0.02) μA, respectively. The variation of Pd/n-Ge (100) Schottky diodes barrier height between 100-500°C is approximately constant within experimental error. According to Gaudet et al [14], only one germanide phase, PdGe exist for Pd on *n*-Ge (100) in this temperature range. This germanide is stable over a wide range of temperature.
The value of ideality factor for as-deposited Pd/n-Ge (100) diodes was determined to be 1.14. The ideality factors were between 1.20 and 1.50 at annealing temperatures between 25°C and 525°C.

The variation of SBH and reverse current at a bias of voltage -1 V with annealing temperature for Ru/n-Ge (100) Schottky diodes is shown in figure 2. The values of SBH and reverse current at -1 V for as deposited Ru/n-Ge (100) Schottky diodes were determined to be (0.557 ± 0.05) eV and (5.79 ± 0.02) μA, respectively. Figure 2 indicates nearly a constant SBH in the temperature range (50-150°C) At annealing temperatures higher than 150°C the SBH decreases with annealing temperature reaching a low SBH of (0.467 ± 0.005) eV after a 275°C anneal, depicting a significant reaction between Ru and the Ge substrate forming a germinide Ru+Ru_2Ge_3 [14]. We propose that, after subjecting the Ru Schottky diodes on n-Ge (100) to isochronal annealing, the first phase of Ru germanide is formed in the temperature range 150-275°C, as the SBH decreases significantly above 150°C annealing. The increase in SBH after annealing at temperatures in the range 325-525°C depicts the formation of the Ru germinide Ru_2Ge_3 [14]. After a 550°C the diodes became near-ohmic and further evaluation was impossible. The as-deposited ideality factor for the Ru/n-Ge (100) Schottky diodes was found to be 1.08. This ideality factor is almost a constant within experimental error up to annealing temperature of 175°C. The ideality factor was greater than 1.1 for annealing temperatures higher than 175°C.

The interface states and chemical reactions between metals and semiconductors at the interface play an important role in the electrical properties of devices [15]. Since during the annealing process, metals may react with semiconductors and new compounds would form. Therefore, the change in SBHs may be attributed to the combined effects of interfacial reaction and phase transformation [15].

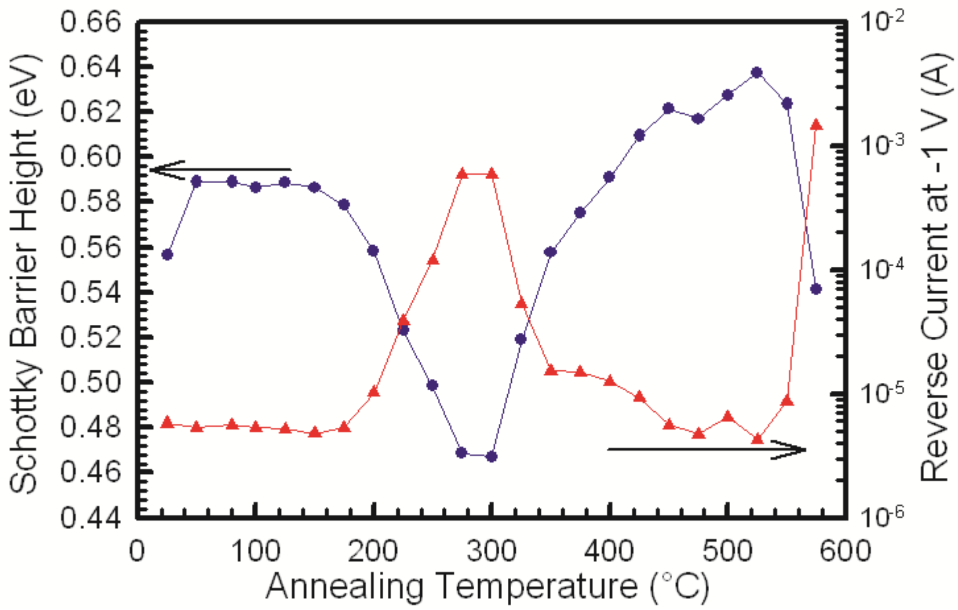
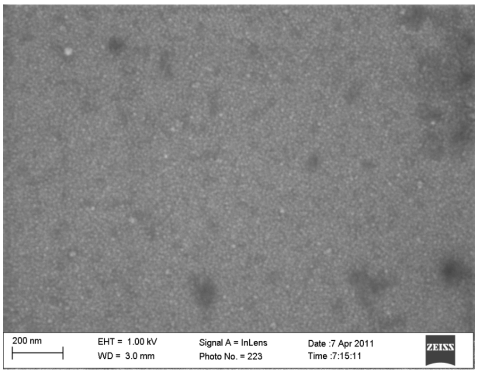


Figure 2. Plot of the Schottky barrier height and reverse current at -1 V as a function of annealing temperature for Ru Schottky contacts on *n*-Ge (100).

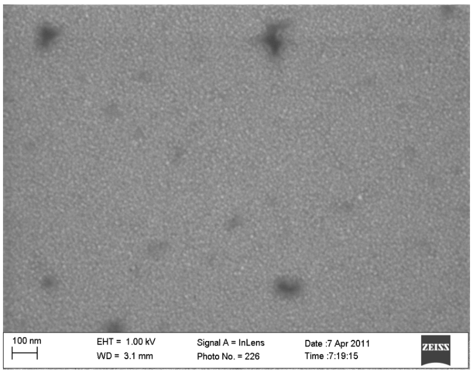
For ideal Schottky diode the ideality is 1.0. The deviation from ideality may be due mostly to the states associated with the defects near the surface. Interface states, inter-diffusion, compound formation, etc can all be derived from thermodynamics due to thermal annealing [16]. These may lead to recombination centres [17], and SBH inhomogeneities [18], which may cause a flow of excess current leading to a deviation from the ideal TE behavior.

Scanning electron microscopy (SEM) observations were conducted for Pd/- and Ru/*n*-Ge (100) samples, as-deposited and annealed at different temperatures. Results are shown in figures 3 and 4. Figure 3 shows the morphological evolution of Pd films on *n*-Ge (100). In figure 3 (a) and (b) the metal surface shows little change when annealed below 400°C. Grain growth at the surface was evident after 400°C anneal and severe grain grooving was observed after a 600°C anneal (Figure 3 (e)). From these results we suggest a good morphological stability for Pd films on *n*-Ge (100). From these observations we conclude that the onset temperature for agglomeration in 30 nm Pd/n-Ge (100) system occurs between 500-600°C.

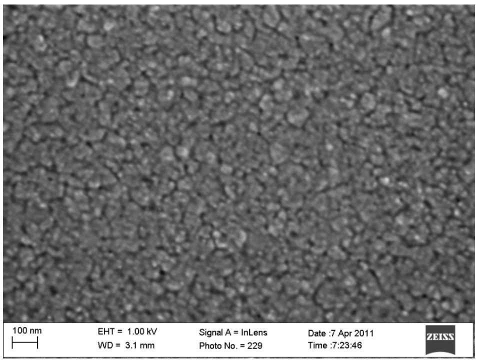
SEM observations of the Ru films on *n*-Ge (100) for as-deposited and morphological evolution of the samples after annealing at different temperatures are shown in figure 4. In figure 4 (a), (b) and (c) the metal surface shows little change when annealed below 500°C. Grain growth was evident after 600°C anneal (Figure 4. (d)). After annealing at 700°C (see figure 4 (e)), film continuity was interrupted as indicated by dark spots caused by exposed Ge regions. It can be concluded from these SEM micrographs that the onset temperature for agglomeration in 30 nm Ru/*n*-Ge (100) system is between 600-700°C.



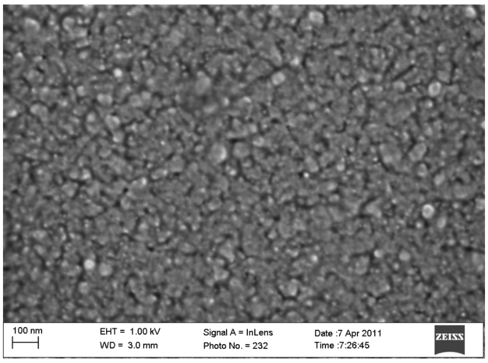
(a)



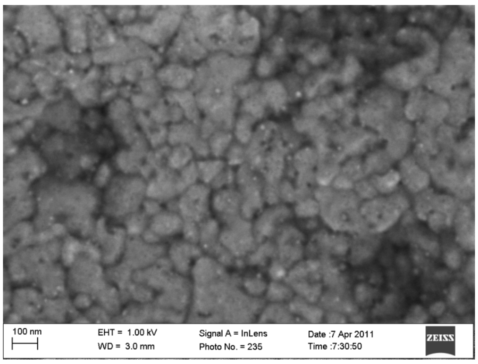
(b)



(c)

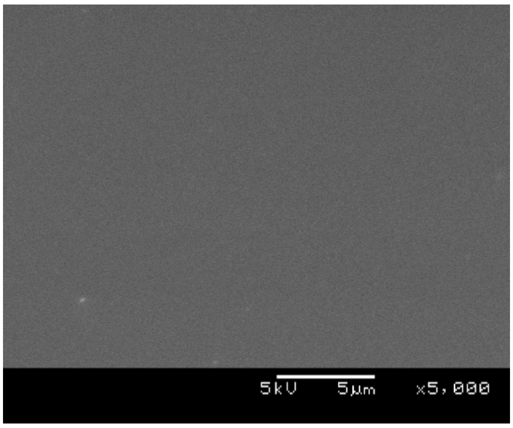


(d)

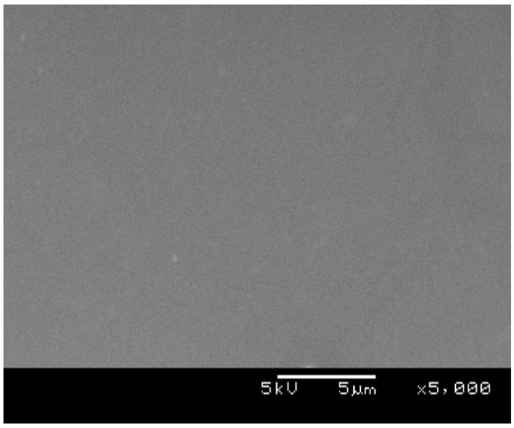


(e)

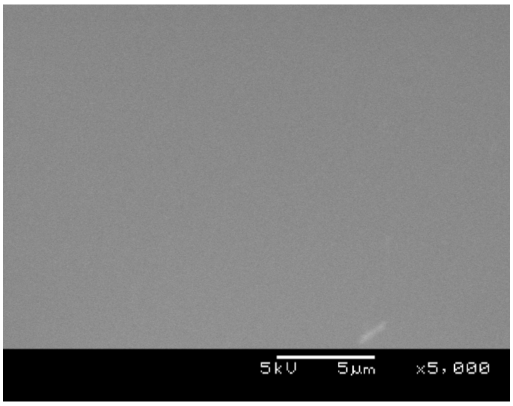
Figure 3. SEM observation for Pd films deposited on n-Ge (100) after isochronal thermal treat at different annealing temperatures: (a) as-deposited, (b) 200 (c) 400 (d) 500 and (e) 600°C



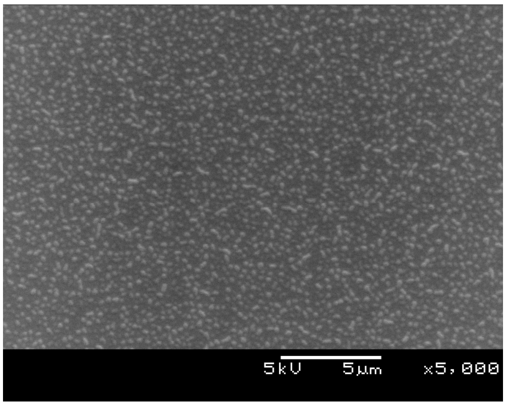
(a)



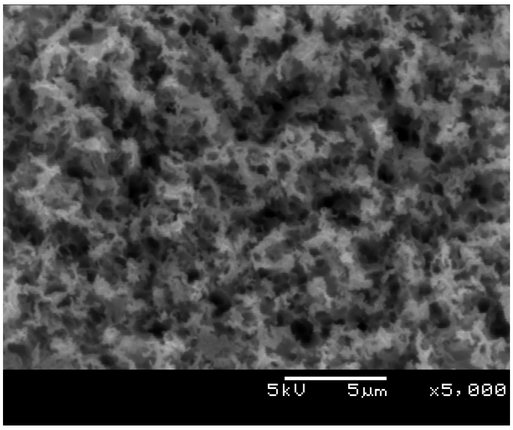
(b)



(c)



(d)



(e)

Figure 4. SEM observation for Ru films deposited on germanium after isochronal thermal treat for 30 min at different annealing temperatures: (a) as-deposited, (b) 400, (c) 500, (d) 600 and (e) 700°C.

4. Summary and Conclusions

Pd/n-Ge (100) Schottky diodes were fabricated by resistive deposition. Ru/n-Ge (100) diodes were fabricated by electron beam deposition. The Schottky behaviour was investigated under various annealing conditions. SEM observations were carried out for samples annealed at different temperatures. The variation of SBHs and ideality factors with annealing temperature may be due to interfacial reactions of Pd and Ru with germanium and the phase transformation of metal-germanides during annealing process. The results show that Pd/- and Ru/n-Ge (100) Schottky diodes are thermally stable over a wide range of temperatures. From SEM observations, it can be concluded that the onset temperature for agglomeration in Pd/n-Ge(100) system occurs between 500-600°C, and in Ru/n-Ge (100) system occurs between 600-700°C.

Acknowledgements

This work has been made possible by financial assistance from South African National Research Foundation.

References

[1] Ashburn S P, Öztürk M, Harris G and Maher M 1993 *J. Appl. Phys.* **74** 4455
[2] An X, Fan C, Huang R and Zhang X 2009 *Chin. Phys. Lett.* **26** 087304
[3] Sun H P, Chen Y B, Pan X Q, Chi D Z, Nath R and Floo Y L 2005 **86** *Appl. Phys. Lett.* 071904
[4] Chi D Z, Yao H B, Liew S L, Tan C C, Chua C T, Chua K C, Li R and Lee S J 2007 *International Workshop on Junction Technology* Technology 81
[5] Chui C O, Ramanathan, Triplett B B, McIntyre P C and Saraawat K C 2002 *IEEE Electron Dev. Lett.* **23** 473
[6] Zhang S L and Ostling M 2003 *Crit. Rev. Solid State Mater. Sci.* **28** 1
[7] Tung R T 2001 *Mater. Sci. Eng. R* **35** 1
[8] Yüksel Ö F 2009 *Physica B* **404** 1993
[9] Sze S M 1981 *Physics of Semiconductor Devices* (New York: Wiley- Interscience)
[10] Wermer J H and Güttler H H 1991 *J. Appl. Phys.* **69** 1522
[11] Chand S and Kumar J 1996 *J. Appl. Phys.* **80** 288
[12] Yahia I S, Fadel M, Sark G B, Yakuphanoglu, Shenouda S S and Farooq W A 2011 *J. Alloys Compd.* **509** 4414
[13] Uslu H, Altindal S, Aydemir U, Dokme I and Afandiyeva 2010 *J. Alloys Compd.* **503** 96
[14] Gaudet S, Kellock, Desjardins P and Lavoie C 2006 J. Vac. Sci. Technol. A **24** 474
[15] Sun Y, Shen X M, Wang J, Zhao D G, Feng G, Fu Y, Zhang S M, Zhang Z H, Feng Z H, Bai Y X and Yang H 2002 *J. Phys. D: Appl. Phys.* **35** 2648
[16] Sands T 1988 *Appl. Phys. Lett.* **52** 197.
[17] Dogan H, Yildirim N, Turut A 2008 *Microelectron. Eng.* **85** 197
[18] Tung R T, Sullivan J P, Schrey F 1992 *Mater. Sci. Eng.* **14** 266