Thermal annealing behaviour of Pd Schottky contacts on Melt-Grown Single crystal ZnO studied by *IV* and *CV* measurements

W. Mtangi[1*], F. D. Auret[1], A. Chawanda[1], P. J. Janse van Rensburg[1], S. M. M Coelho[1], J. M. Nel[1], M. Diale[1], L. van Schalkwyk[1], C. Nyamhere[2].

[1]*Department of Physics, University of Pretoria, Private bag X20, Hatfield, 0028, South Africa.*
[2]*Department of Physics, P.O. Box 77000, Nelson Mandela Metropolitan University, Port Elizabeth 6031, South Africa.*

Abstract

The effects of ZnO annealing have for the first time been investigated on the rectification behaviour of highly rectifying Pd Schottky contacts deposited on ZnO using the current-voltage (*IV*) and capacitance-voltage (*CV*) measurement techniques. *IV* results reveal a decrease in the contact quality with increasing annealing temperature as confirmed by a decrease in the zero bias barrier height and an increase in the reverse current measured at -1.5 V. An average barrier height of (0.77 ± 0.02) eV has been calculated by assuming pure thermionic emission for the as-deposited material and as (0.56 ± 0.03) eV after annealing at 550°C. The reverse current has been measured as (2.10 ± 0.01) × 10^{-10} A for the as-deposited and increases by 5 orders of magnitude after annealing at 550°C to (1.56 ± 0.01) × 10^{-5} A. The depletion layer width measured at –2.0 V has shown a strong dependence on thermal annealing as it decreases from 1.09 μm after annealing at 200°C to 0.24 μm after annealing at 500°C, resulting in the modification of the dopant concentration within the depletion region and hence the current flowing through the interface from pure thermionic emission to thermionic field emission with the donor concentrations increasing from 6.90 × 10^{15} cm^{-3} at 200°C to 6.06 × 10^{16} cm^{-3} after annealing at 550 °C. This increase in the volume concentration has been explained as an effect of a conductive channel that shifts closer to the surface after sample annealing [1]. The series

* Corresponding author. Email address: wilbert.mtangi@up.ac.za, Phone: +27 12 420 2684

resistance has been observed to decrease with increase in annealing temperature. The Pd contacts have shown high stability up to an annealing temperature of 250 °C as revealed by the *IV* and *CV* characteristics after which the quality of the contacts deteriorates with increase in annealing temperature.

Keywords: Thermal annealing, Pd/ZnO Schottky, depth profile, surface conduction, Barrier height

Introduction

ZnO is a wide bandgap material with many applications in the fabrication of optoelectronic devices that can operate in the UV region. Since ZnO is a material that is resistant to radiation damage [2], it is a good candidate for use in satellites situated in space. The use of ZnO in space applications requires the material to withstand variations in high temperatures to some extent, hence the need to investigate the variation in the electrical properties of the material devices with temperature. Effects of high temperature annealing on ZnO have been studied using Hall Effect measurements [1, 3, 4, 5]. Results from these studies indicate the existence of a conductive channel that tends to dominate current flow at low temperatures when the bulk carriers are frozen to their donor atoms. Modelling of the Hall effect results indicates an increase in the surface volume concentration with increase in annealing temperature [1]. Fabrication of good rectifying contacts with high Schottky barriers, low ideality factors and low leakage currents has always been a challenge since the earliest surface studies [6], until of late where researchers have used chemical treatments some, of which include hydrogen peroxide to realise good quality Schottky contacts on ZnO [7, 8, 9, 10, 11] with very low leakage currents. To our knowledge, there is not much detail on the high temperature annealing behaviour and surface effects on metal ZnO contacts. The limiting factor could be the quality of the contacts as the leakage currents that have been measured are quite high to allow for high temperature annealing as this leads to the degradation of the contacts [12]. An increase in leakage currents leading to the degradation of the contact quality has been reported [13, 14, 15]. Ip *et al*. [13] studied the effects of annealing Pt contacts in the 25 to 100°C temperature range in which they reported an increase in saturation current density of 1.53×10^{-4} Acm^{-2} (25 °C) to 6.03×10^{-2} Acm^{-2} (100 °C), while Ghusoon *et al*. [15] studied the effects of thermal treatment on ZnO-based metal-insulator-semiconductor photodetectors up to an annealing temperature of 250°C. Their results indicate a drastic degradation of device performance after annealing at 250°C. Brillson *et al*. [14] have also studied the surface passivation and Schottky barrier formation at ZnO surfaces and interfaces. They reveal a decrease in the rectification behaviour of their contacts after annealing at 650°C with the reverse current increasing from approximately 1 x 10^{-5} A for the as-deposited sample to 1 x 10^{-3} A after annealing at 550°C. In this study, the thermal annealing effects are systematically investigated on the rectification behaviour of Pd Schottky contacts deposited on ZnO using the current-voltage (*IV*) and capacitance-voltage (*CV*) measurement techniques.

Experimental

Pd Schottky contacts of diameter 0.6 mm and thickness 100 nm were resistively deposited on the O-polar face of bulk single crystal ZnO of orientation (0001) obtained from Cermet Inc. Sample preparation was done as described by [10]. The samples were then annealed for 30 minutes in Ar ambient. Room temperature dark *IV* and *CV* measurements were then performed. Isochronal annealing was performed on the same sample under an Ar atmosphere followed by *IV* and *CV* measurements in the temperature range 200 – 550 °C in 50°C steps for a period of 10 minutes.

Results and discussion

Fig. 1 shows the semi-logarithmic *IV* characteristics of the Pd Schottky contacts deposited on ZnO. The as-deposited sample shows a high rectification behaviour with a reverse current of 2.10×10^{-10} A at −1.5 V. As the annealing temperature increases to 550°C, the reverse current increases by approximately 5 orders of magnitude to 1.56×10^{-5} A . It should be noted that the reverse current increases by approximately one order of magnitude after every annealing cycle as shown in Table 1. The low leakage current observed for the as-deposited sample could be due to surface passivation by hydrogen peroxide treatment as explained by Schifano *et al.* [16]. The increase in leakage current with annealing is due to a decrease in the depletion layer width after annealing that will result in changes in the current transport processes across the interface from conventional thermionic emission to enhanced tunnelling and also defect induced changes in doping within the depletion region after high temperature annealing. This has also been explained by Brillson *et al.* [14]. Fig. 2 shows an increase in capacitance with annealing temperature in the voltage range examined which is substantial evidence of depletion width lowering, as our capacitance depends on the depletion layer width if we treat the metal-semiconductor contact as a parallel plate capacitor and the depletion region as the dielectric of the capacitor. The capacitance will be given by:

$$C = \frac{\varepsilon_s A}{w} \qquad (1)$$

where ε_s is the semiconductor dielectric constant, *A* is the diode cross sectional area and *w* is the depletion width given by,

$$w = \sqrt{\frac{2\varepsilon_s V_d}{qN_D}} \qquad (2)$$

The capacitance can be given by

$$C = \sqrt{\frac{qN_D \varepsilon_s}{2V_d}} A \qquad (3)$$

where qN_D is the volume charge density that can be obtained from the graph of $1/C^2$ versus V_d plot (not shown) and V_d is the voltage across the diode.

The depletion layer width obtained from equation (2) is plotted as a function of annealing temperature in Fig. 3, together with the donor concentration obtained at -2.0 V. The thickness of the depletion region has been calculated at -2.0 V together with the corresponding donor concentration as 1.09 μm and 6.90 × 10^{15} cm^{-3}, respectively after annealing at 200°C. Both the thickness and the donor concentration stay almost constant up to an annealing temperature of 250°C. This indicates that the contacts are stable within the 200 – 250°C temperature range. This is also indicated by a small change in the *IV* and *CV* characteristics of the contacts. After annealing at 300°C, a significant decrease in the depletion layer width from approximately 1.09 μm to 0.24 μm is observed together with a change in the calculated donor concentration from 5.00 × $10^{15}$$cm^{-3}$ to 6.06 × 10^{16} cm^{-3} after annealing at 550°C. This could be due to the fact that after annealing at 300°C, some neutral shallow donors become thermally activated causing an increase in the dopant concentrations [1, 14], hence influencing the thickness of the depletion region. These changes in dopant concentrations within the depletion region cause a change in the dielectric constant of the semiconductor and in turn affect the measured capacitance. After annealing at 500°C, the depletion width thickness becomes almost constant with increase in annealing temperature. Similarly the donor concentration measured at -2.0 V also becomes constant within this region. Fig. 4 shows the depth profile as a function of annealing temperature as determined using the *CV* technique. The maximum depth probed at -2.0V decreases with increasing annealing temperature. The donor concentration measured within the probed region is constant up to annealing temperature of 250°C. It shows a significant increase with annealing temperature and shifts very close to the metal-semiconductor interface after annealing at 300°C until 500°C where it becomes constant with annealing. This increase in carrier concentration closer to the surface supports enhanced tunnelling of carriers resulting in high leakage currents of the contacts.

Another explanation of an increase in the leakage current could be due to an increase in surface conduction with annealing. The existence of surface conduction in ZnO has been explained by [3, 17, 18]. Even though hydrogen peroxide passivates the surface of ZnO, it has been previously demonstrated that high temperature annealing causes an increase in surface conduction even for the peroxide treated samples from Hall effect studies [1]. This surface conduction provides an easy path for current flow even when the contact is reverse biased resulting in large currents flowing under reverse bias for high temperature annealed contacts as was also explained by Oh *et al*. [19]. The forward *IV* characteristics of the contacts indicate two distinct regions. The upper part of the curves is affected by the series resistance effect. The series resistance has been observed to decrease with increase in annealing temperature as shown in Table 1. The lower region of the curves has been modelled by assuming pure thermionic emission, where the current flowing through the metal-semiconductor contact can be estimated by [19],

$$I = I_0 \left[exp\left(\frac{qV}{kT}\right) - 1 \right] \quad (4)$$

where n is the ideality factor, k is the Boltzmann constant, T is the Kelvin temperature and I_0 is the saturation current obtained as the intercept of the current axis, i.e. when $V = 0$ V and is defined by,

$$I_0 = AA^{*}T^2 exp\left(-\frac{q\Phi_{b0}}{nkT}\right) \quad (5)$$

where A is the Schottky contact area, A^* is the effective Richardson constant estimated to be $32\ AK^2cm^{-2}$ and ϕ_{b0} is the zero bias barrier height obtained at $V = 0V$ and is given by,

$$\phi_{b0} = \frac{kT}{q} ln\left(\frac{AA^*}{T^2}\right) \qquad (6)$$

Fig. 5 shows the variation of the reverse current at -1.5 V and zero bias barrier height with annealing temperature. The barrier height decreases with annealing temperature while the reverse current increases with annealing temperature. This is the most expected trend as carriers are now able to tunnel through the barrier after high temperature anneals while others are contributing to current flow across the interface through surface conduction even under large reverse biasing. The decrease in zero bias with annealing temperature can be explained by the increase in saturation current with temperature shown in Fig. 6. Without biasing, carriers are in thermal agitation and can tunnel through the barrier as the depletion region is now thinner. It must be noted that the saturation current values in Fig. 6 are the ones that have been used to calculate the zero bias barrier height using equation (6). The calculated barrier height decreases from 0.77 eV for the as-deposited sample to 0.56 eV after annealing at 550°C.

Conclusions

We have successfully fabricated and characterized Pd Schottky contacts on ZnO with low leakage currents that allowed *IV* and *CV* measurements up to 550°C. The contacts have revealed a decrease in zero bias barrier height from 0.77 eV for the as-deposited to 0.56 eV after annealing at 550°C while the reverse current increases by 5 orders of magnitude from 2.10×10^{-10} A for the as-deposited to 1.56×10^{-5} A after annealing at 550°C. This increase in reverse current has been explained as due to surface conduction with the donor concentration increasing from 6.90 × 10^{15} cm^{-3} after annealing at 200°C to 6.06 × 10^{16} cm^{-3} after annealing at 550°C and reduction in the depletion width of the metal-semiconductor interface as revealed by the *CV* measurements from 1.09 μm on the as-deposited to 0.24 μm after annealing at 550°C, resulting in the modification of the dopant concentration within the depletion region and hence the current flowing through the interface from pure thermionic emission to thermionic field emission.

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Table 1: Values of ideality factor n, reverse current and series resistance as a function of annealing temperature for the Pd Schottky contacts on ZnO.

Temperature (°C)	Ideality factor, n	Current at -1.5 V(A)	Series resistance (Ω)
as deposited	1.85	2.10E-10	43.05
200	2.21	4.12E-09	50.59
250	2.11	9.65E-09	49.89
300	2.31	6.18E-08	37.03
350	2.14	1.17E-07	28.24
400	2.61	4.82E-06	27.34
450	2.89	1.76E-06	50.98
500	2.40	2.80E-05	194.02
550	2.04	1.56E-05	219.80

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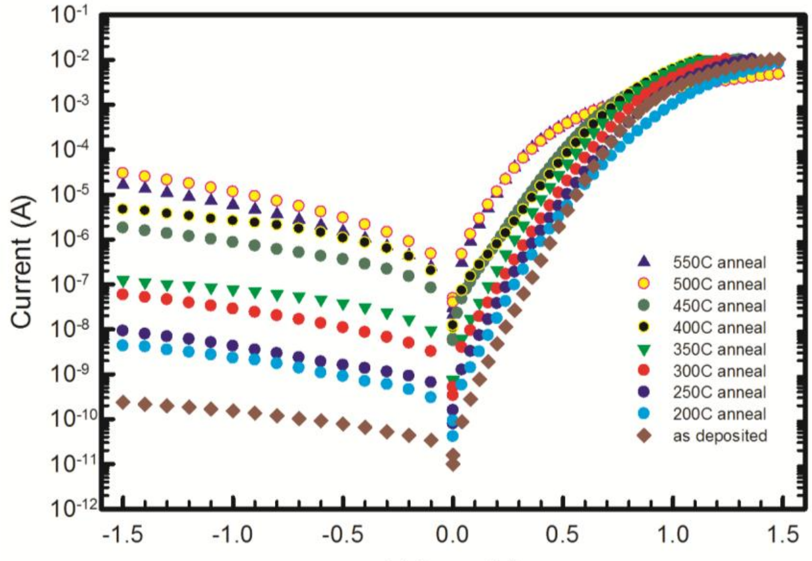

Figure 1

Fig. 1: (Colour on line) Semi-logarithmic *IV* plot for the Pd/ZnO Schottky contacts annealed at 200°C to 550°C in an argon ambient.

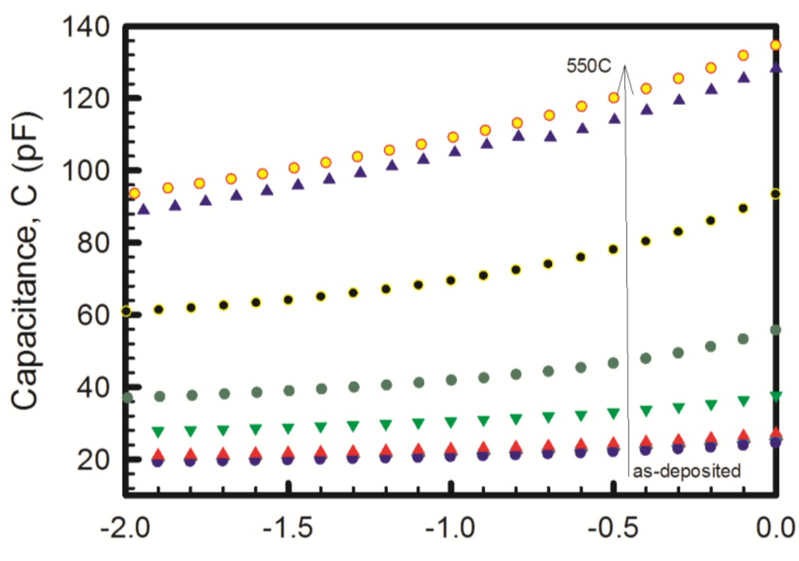

Figure 2

Fig. 2: (Colour on line) The *CV* characteristics of the Pd/ZnO Schottky contacts annealed at 200°C to 550°C in an argon ambient. The arrow indicates an increase in annealing temperature.

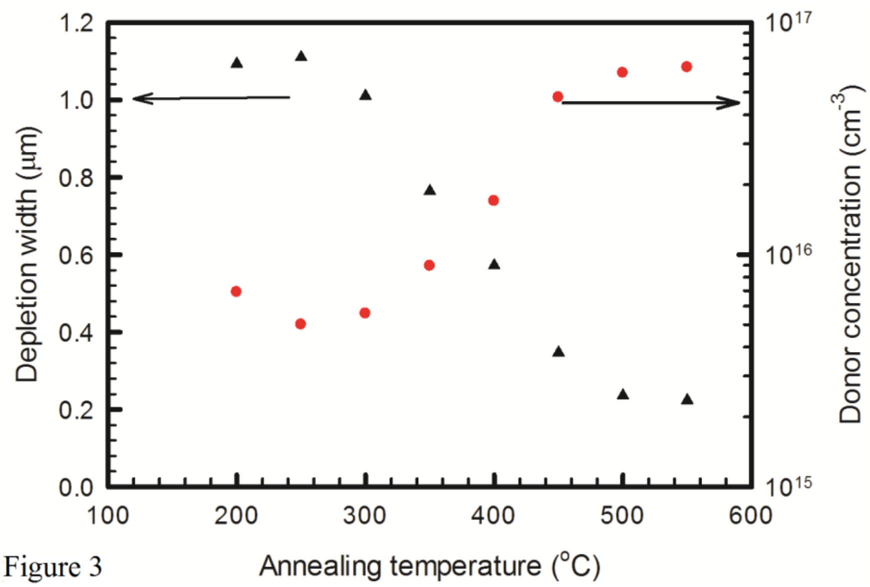

Figure 3

Fig. 3: (Colour on line) The variation of depletion width (triangles) and donor concentration (circles) with annealing temperature.

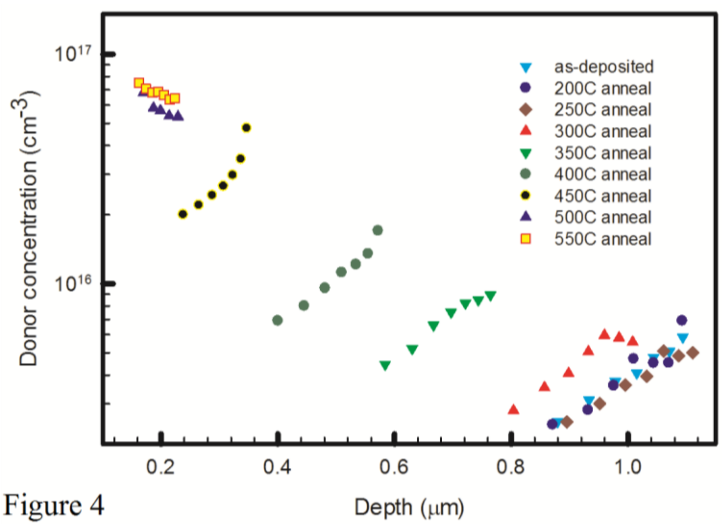

Figure 4

Fig. 4: (Colour on line) The variation of donor concentration with depth for the Pd/ZnO Schottky contacts annealed at 200°C to 550°C in an argon ambient.

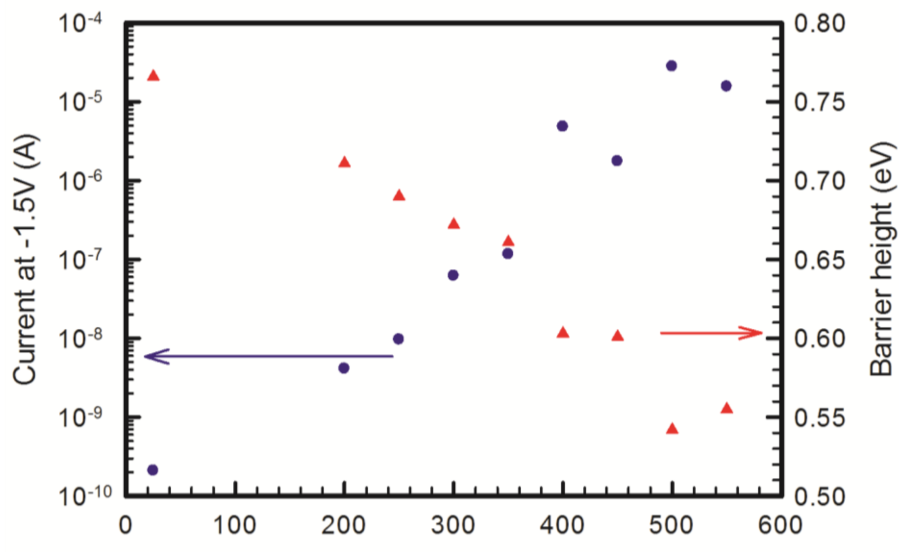

Figure 5

Fig. 5: (Colour on line) The variation of reverse current at -1.5 V (circles) and barrier height (triangles) with annealing temperature.

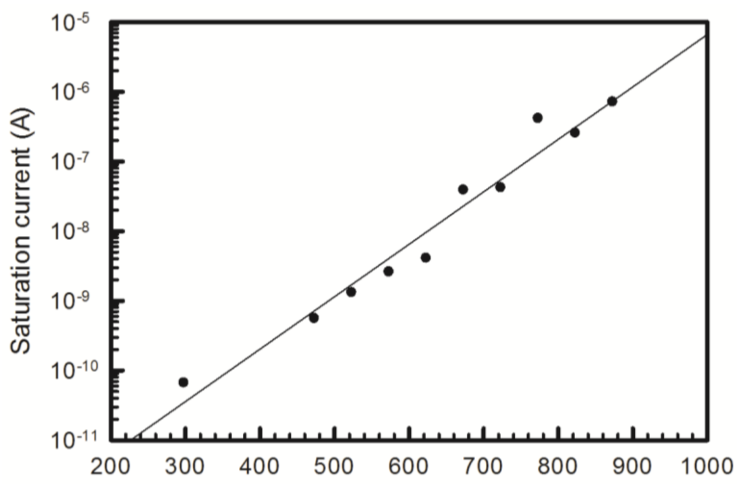

Figure 6

Fig. 6: Shows the variation of saturation current with annealing temperature for the Pd/ZnO Schottky contacts.