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Thermal stability study of palladium and cobalt Schottky contacts on n-Ge (1 0 0) and defects introduced during contacts fabrication and annealing process

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ABSTRACT

Palladium (Pd) and cobalt (Co) Schottky barrier diodes were fabricated on n-Ge (1 0 0). The Pd-Schottky contacts were deposited by resistive evaporation while the Co-contacts were deposited by resistive evaporation and electron beam deposition. Current–voltage (*I–V*), capacitance–voltage (*C–V*) and deep level transient spectroscopy (DLTS) measurements were performed on as-deposited and annealed samples. Electrical properties of Pd and Co samples annealed between 30 and 600 °C indicate the formation of one phase of palladium germanide and two phases of cobalt germanide. No defects were observed for the resistively evaporated as-deposited Pd-and Co-Schottky contacts. A hole trap at 0.33 eV above the valence band was observed on the Pd-Schottky contacts after annealing at 300 °C. An electron trap at 0.37 eV below the conduction band and a hole trap at 0.29 eV above the valence band was observed on as-deposited Co-electron beam deposited Schottky contacts. Rutherford back scattering (RBS) technique was also used to characterise the Co–Ge, for as-deposited and annealed samples.

1. Introduction

Microelectronics has been primarily a Si-based technology because of the stability and high quality of SiO_2 and its interface with a Si substrate [1]. Attempts to develop faster devices in modern microelectronics have increased the interest for alternative materials to silicon, compatible with the existing silicon-based technology [2]. Germanium (Ge) is often proposed as a potential alternative to silicon due to its high carrier mobility, low effective mass of holes [3] and relative compatibility with silicon processing. This has led to renewed interest in the complete understanding of metal–germanium interactions and dynamic properties of radiation and process-induced defects in Ge.

In this work, palladium (Pd) and cobalt (Co) Schottky contacts on n-Ge (1 0 0) were fabricated and electrical properties of the contacts were investigated. We also report the electronic properties of defects introduced during contacts fabrication and annealing process. The in-diffusion of Co–Ge was investigated by employing Rutherford backscattering spectroscopy.

2. Experimental procedure

We have used bulk grown n-type Ge with (1 0 0) crystal orientation, doped with antimony, (Sb) to a density of 2.5×10^{15} cm^{-3} supplied by Umicore. Before metallization the samples were first degreased and then etched in a mixture of H_2O_2:H_2O (1:5) for 1 min. Immediately after cleaning they were inserted into a vacuum chamber where AuSb (0.6% Sb), 120 nm thick, was deposited by resistive evaporation as back ohmic contacts. Anneal at 350 °C for 10 min 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 contacts were deposited by vacuum resistive evaporation and the Co contacts were deposited by vacuum resistive evaporation and electron beam deposition. The contacts were 0.6 mm in diameter and 30 nm thick. After the contact formation the samples were characterized by current–voltage (*I–V*) and capacitance–voltage (*C–V*) measurements at room temperature to determine the quality of the diodes. The electrical characterization was repeated after every annealing cycle in Ar gas for 30 min between 30 and 600 °C. The defects introduced were characterised by DLTS [4] and LDLTS [5,6]. The '*signatures*' of induced defects (i.e. energy position in band gap relative to the conduction band and valence band for the electron traps and hole traps, respectively, E_T, and their apparent capture cross section, σ_a), were determined from Arrhenius plots of

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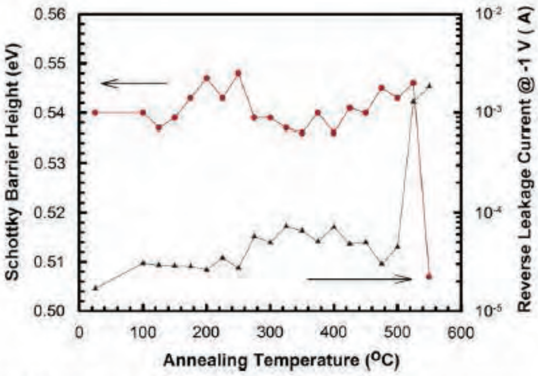

Fig. 1. (Color online) Plot of the Schottky barrier height and the Reverse leakage current at −1 V as function of annealing temperature for Pd Schottky contacts on n-Ge (1 0 0).

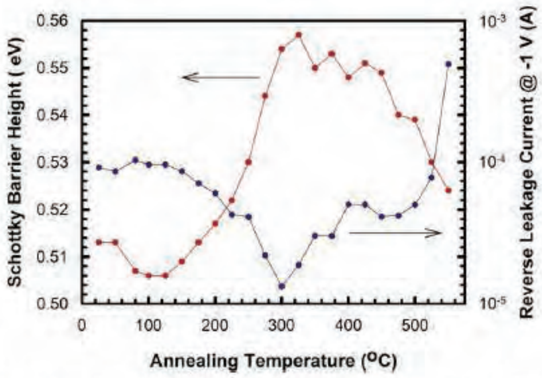

Fig. 2. (Color online) Plot of the Schottky barrier height and the Reverse leakage current at −1 V as a function of annealing temperature for Co Schottky contacts on n-Ge (1 0 0).

$\ln(T^2/e)$ vs. $1000/T$, where 'e' is either the hole or electron emission rate, and T is the measurement temperature [7].

Rutherford backscattering spectroscopy (RBS) with beam energy of 1.6 MeV He ions and a solid-state detector positioned at $\theta = 165^\circ$ relative to the incident beam, was used to analyze the Co–Ge in diffusion in the samples, as-deposited, and after annealing at 325, 425, 500 and 600 °C.

3. Results and discussion

3.1. Germanides formation

Fig. 1 shows the variation of the Schottky barrier height and reverse current at −1 V with annealing temperature for the Pd Schottky contacts. Fig. 3(a) shows the variation of Pd Schottky contacts ideality factor with annealing temperature. From Figs. 1 and 3(a), the electrical properties of the Pd Schottky contacts between 250 and 500 °C annealing temperature, we propose that one phase of palladium germanide, PdGe is formed and is stable over a wide temperature range. This is in agreement with what was observed by Gaudet et al. [1].

The variation of the Schottky barrier height, reverse leakage current at −1 V and ideality factor with annealing temperature for the Co Schottky contacts is shown in Figs. 2 and 3(b). The variations of these electrical parameters with annealing temperature suggest that three phases of Co germanides are formed. We propose that CoGe, Co_5Ge_7 and $CoGe_2$ germanides are formed during the annealing process. The CoGe formed between 100 and 300 °C, Co_5Ge_7 formed around 300 °C and then transform to $CoGe_2$ at temperature above 425 °C [8].

3.2. DLTS analysis of fabrication and annealing process induced defects

Fig. 4 shows a conventional DLTS spectrum obtained from Pd Schottky contacts annealed from room temperature to 350 °C. It depicts that no defects are observable for the resistively evaporated as-deposited Pd Schottky contacts and a hole trap E_V+0.33 eV labeled $H(0.33)$ with capture cross-section of $1.02 \times 10^{-14}\,\text{cm}^{-2}$ was observed after annealing at 300 °C. We speculate that this defect is probably Pd related.

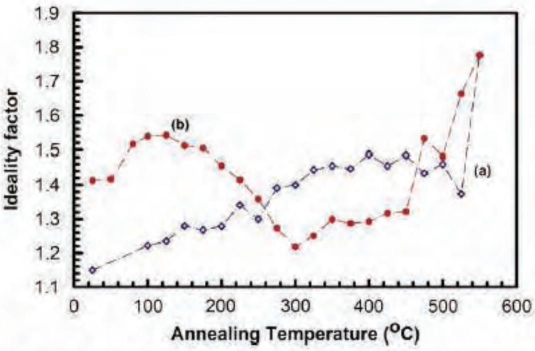

Fig. 3. (Color online) Plot of Ideality factor as a function of annealing temperature for: (a) Pd Schottky contacts on n-Ge (1 0 0) and (b) Co Schottky contacts on n-Ge (1 0 0).

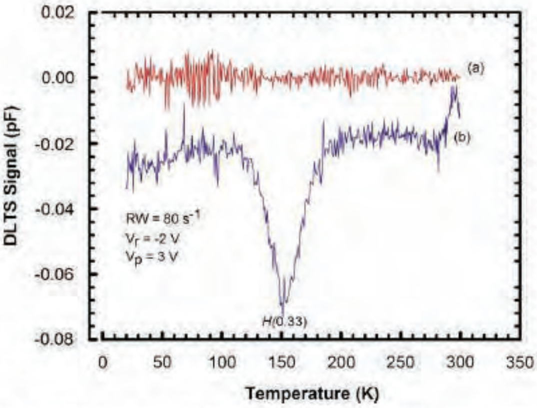

Fig. 4. DLTS spectra of the Pd Schottky contacts on n-Ge (1 0 0) (a) as-deposited and (b) after annealing at 300 °C. These spectra were recorded at a rate window of $80\,\text{s}^{-1}$ and quiescent reverse bias of −2 V with a filling pulse of 3 V.

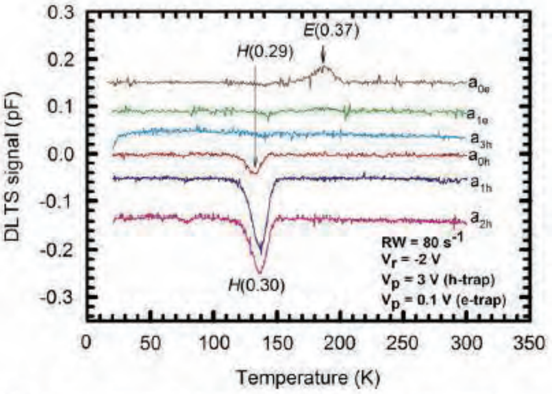

Fig. 5. DLTS spectra of the EBD Co Schottky contacts on n-Ge (100) (a_0) as-deposited and after annealing at (a_1) 200 °C, (a_2) 300 °C and (a_3) 350 °C. The subscripts '*e*' and '*h*' on the graph labels stand for electron and hole traps. These spectra were recorded at a rate window of $80\,s^{-1}$ and quiescent reverse bias of −2 V with a filling pulse of 0.1 and 3 V for an electron and a hole trap, respectively.

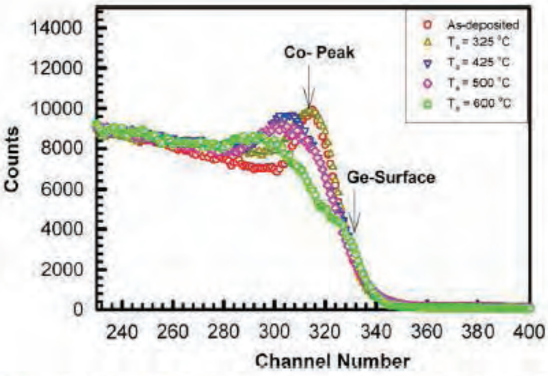

Fig. 6. (Color online) Backscattering energy spectra of 1.6 MeV He^+ ions for cobalt films deposited on germanium after isochronal thermal treatment for 30 min at different annealing temperatures: as-deposited, 325, 425, 500 and 600 °C.

An electron trap at E_C+0.37 eV labeled *E*(0.37), and a hole trap at E_V+0.29 eV with capture cross sections of $4.03\times10^{-14}\,cm^{-2}$ and $3.03\times10^{-14}\,cm^{-2}$, respectively were observed in as-deposited, Co Schottky contacts fabricated with electron beam deposition (EBD), as shown in Fig. 5. The electron trap *E*(0.37) is the well known (=/−) charge state of the *E*-center (V–Sb) in Sb-doped Ge [9], whilst the hole trap *H*(0.29) is the (−/0), the single acceptor level of the Sb–V center in Ge. The hole trap *H*(0.29) is thermally stable up to an annealing temperature of 150 °C and anneals out at 200 °C [7]. Further annealing studies in the temperatures ranging from 200 to 350 °C, reveal a hole trap *H*(0.30), shown in Fig. 5 with capture cross section of $7.8\times10^{-14}\,cm^{-2}$ and anneals out between 300 and 350 °C. A similar defect *H*(0.30) was also observed by Nyamhere et al. [10] during the characterization of defects introduced in antimony doped germanium by 3 keV Ar sputtering. We speculate that this hole trap is a vacancy related defect, formed when vacancies are injected into the Ge substrate during the metal germanidation process.

From the DLTS characterization of the resistively evaporated Co Schottky contacts, no defects were observed in the as-deposited samples and samples annealed up to 600 °C.

3.3. *RBS analysis on the Co–Ge samples*

Fig. 6 shows the RBS spectra of the Co–Ge samples; as-deposited, annealed at 325, 425, 500 and 600 °C. From Fig. 6 it is shown that Co is diffusing into Ge from the low annealing temperature (325 °C). The Co is presumed to start diffusing into Ge at a temperature of 150 °C as reported by Sun et al [8]. Co atoms will diffuse into bulk Ge at a relatively low temperature of (~150 °C). The diffusion is dominant as annealing temperature increases to 500 °C. At 600 °C, Co has significantly diffused into Ge.

4. Summary

Pd- and Co-germanides were fabricated by resistive deposition and electron beam deposition followed by an annealing process. The electrical properties of the Pd Schottky contacts show that one phase of palladium germanide, PdGe was formed. CoGe, Co_5Ge_7 and $CoGe_2$ are the three cobalt germanides we propose to have formed during the Co Schottky contacts annealing process. Annealing studies of the Pd Schottky contacts reveal the introduction of a hole trap *H*(0.33) at a temperature of 300 °C. This hole trap is probably Pd related as a similar hole trap was not observed during the annealing studies of EBD Co-Schottky contacts. DLTS analysis on the EBD Co-Schottky contacts has shown that an electron trap *E*(0.37) and a hole trap *H*(0.29) were induced during the fabrication of the contacts and a hole trap *H*(0.30) is induced during the annealing process.

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References

[1] S. Gaudet, A.J. Kellock, P. Desjardins, C. Lavoie, J. Vac. Sci. Technol. A 24 (3) (2006) 474.
[2] V.I. Kolkovsky, M. Christian Petersen, A. Nylandsted Larsen, Appl. Phys. Lett. 90 (2006) 112110.
[3] F.D. Auret, W.E. Meyer, S. Coelho, M. Hayes, Appl. Phys. Lett. 88 (2006) 242110.
[4] D.V. Lang, J. Appl. Phys. 45 (1974) 3023.
[5] L. Dobaczewski, P. Kaczor, I.D. Hawkins, A.R. Peaker, J. Appl. Phys. 76 (1994) 194.
[6] L. Dobaczewski, A.R. Peaker, K.B. Nielsen, J. Appl. Phys. 96 (2004) 4689.
[7] C. Nyamhere, A. Chawanda, A.G.M. Das, F.D. Auret, M. Hayes, Physica B 401–402 (2007) 227.
[8] H.P. Sun, Y.B. Chen, X.Q. Pan, D.Z. Chi, R. Nath, Y.L. Foo, Appl. Phys. Lett. 86 (2005) 071904.
[9] F.D. Auret, S.M. M Coelho, M. Hayes, W.E. Meyer, J.M. Nel, Phys. Stat. Sol. (c) 5 (1) (2008) 160.
[10] C. Nyamhere, et al., Physica B (2009), doi:10.1016/j.physb.2009.09.037.

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Thermal annealing behaviour of platinum, nickel and titanium Schottky barrier diodes on n-Ge (1 0 0)

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ABSTRACT

Platinum (Pt) and titanium (Ti) Schottky barrier diodes were fabricated on bulk grown (1 0 0) Sb-doped n-type germanium using the electron beam whereas nickel (Ni) contacts were fabricated using the resistive evaporation system. Electrical characterization of these contacts using current–voltage (*I–V*) measurements was performed under various annealing conditions. The variation of the electrical properties of these Schottky diodes can be attributed to combined effects of interfacial reaction and phase transformation during the annealing process. The results have also revealed that Pt Schottky contacts are of a high quality, with low reverse currents in the order of (10^{-5} to 10^{-6}) A and as-deposited ideality factors as low as 1.09. Furthermore, the samples microstructural characterization was performed by scanning electron microscopy (SEM) at different annealing temperatures. From the results, it can be concluded that the onset temperature in 30 nm Ni- and Pt/n-Ge (1 0 0) systems occurs at 500–600 °C and 600–700 °C, respectively.

1. Introduction

The solid phase reaction at sub-eutectic temperatures between a thin metal film and a single-crystal semiconductor has attracted much interest because of its importance in Schottky barrier and contact formation, epitaxial growth and device reliability [1]. A good metal-semiconductor (MS) contact is essential for the successful operation of the electronic circuits and devices [2]. Contacts to very large scale integration (VLSI) circuits and interconnections require MS contacts which are thermally stable, have low resistivity and are compatible with the process technology. Due to the shrinking of the advanced Si-based complementary metal-oxide-semiconductor (CMOS) device feature size, new material and device structures to relax the physical limitation in device scaling are now required. Ge has been regarded as the replacement for Si as a channel material in future high-speed CMOS technology, because it offers two times higher intrinsic electron mobility and four times higher intrinsic hole mobility than that of Si [3]. As the possibility of using Ge in microelectronics arises, optimal implementation of germanium technology will require an understanding of metal–germanium interactions from both metallurgical and electrical standpoints.

The reactions of germanium with Pt have been studied [1,4–8], while with Ni have been reported by [4,5,9–15] and with Ti have been investigated [5,16]. The study of the solid state reaction between thin metal films and germanium to determine the phase formation sequence [1,4–6,10–13,15], microstructure of the material [4,5,7,16], growth kinetics [10,15] and electrical characteristics were analyzed by x-ray diffraction [1,4–6,10–13,15,16], Rutherford Backscattering spectroscopy [1], transmission electron microscopy [4,7,10], differential scanning calorimetry [7,10] and current–voltage (*I–V*) [4,6,11,12,14,16], techniques. Yao et al. [4] studied the *I–V* characteristics of Pt/n-Ge (0 0 1) and Ni/n-Ge (0 0 1) after subjecting the Schottky contacts to rapid thermal anneal (RTA) in N_2 ambient at 250–700 °C for 20 s. Gumeniuk et al. [6] have reported the superconductivity in Pt germanides of new skutterditelike compounds MPt_4Ge_{12}. Łaszcz et al. [7] studied the mechanisms of the Pt germanide formation by RTA processes in the Ge/Pt/Ge/SiO_2 structure at 200–600 °C range. Their results depict that, during annealing of the Ge/Pt/Ge/SiO_2 structure at 200 °C the whole Pt layer had reacted with a part of the Ge layer and after 300 °C anneal the whole Ge reacted with Pt. Ohtsu et al. [8] investigated the reactions of the samarium platinum germanides ternary system using high-pressure techniques and a simple arc-melting method. Thanailakis et al. [9] established a relationship between as-deposited Ni/n-Ge (1 1 1) Schottky barrier height value, the metal work function and the density of surface states of the germanium substrate. Peng et al. [11] reported the Ni/n-Ge (1 0 0) Schottky diodes *I–V* characteristics and the nickel germanide induced strain

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after subjecting the Schottky contacts to RTA in the temperature range 300–600 °C. Their results show that the orthorhombic structure of NiGe induces epitaxial tensile strain on Ge substrate due to the difference in the lattice constants. They also suggested that the barrier height increases with increasing annealing temperature may be due to the conduction band edge shift by the strain after germanidation process. An et al. [12] have investigated the impact of ion implantation on nickel germanides formation with pure-Ge substrate and electrical dependence of NiGe/Ge Schottky diodes on contact size. Their results reveal that ion implantation of BF_2 before germanidation is favourable for the formation of low-resistivity monogermanide phase (NiGe). They also showed that the Schottky barrier height of Ni/n-Ge (1 0 0) Schottky diodes formed on pure-Ge substrate decreased with decreasing contact size, while the ideality factor increased remarkably, which may provide the guideline for the application to Schottky source/drain germanium transistors [12]. Peng et al. [13] have carried out micro-Raman studies on nickel germanides formed on (1 1 0) crystalline Ge. From XRD analysis, they found that Ni_5Ge_3, NiGe, and Ni_2Ge phases are formed sequentially with increasing annealing temperatures from 300 °C to 600 °C on n-Ge (1 1 0) substrate. Their results also show a strong tensile stress in the underlying Ge (1 1 0) substrate, which was attributed to the lattice mismatch between nickel germanides and Ge substrate. An et al. [14] have also successfully demonstrated the modulation of Schottky barrier height of Ni/n-Ge (1 1 1) by a germanidation-induced dopant segregation technique. Their results showed that the change of the Schottky barrier height was not attributed to the phase change of nickel germanides but to dopant segregation at the interface of germanides/germanium which causes conduction energy band bending. Perrin et al. [15] have studied both systems (Ni–Si and Ni–Ge) in order to compare their phase formation and growth kinetics. Ni thin films and armorphous semiconductor layers (a-Si and a-Ge) had been deposited on undoped (1 0 0) Si wafers. They have showed that Ni–Si system has three major phases (Ni_2Si, NiSi and $NiSi_2$) that grow sequentially while Ni–Ge system showed only two phases (Ni_5Ge and NiGe) that grow simultaneously. Dedong et al. [16] studied changes in the electrical properties of Ti- and Ni germanide Schottky contacts on n-Ge (1 0 0) substrates in the temperature range 300–500 °C.

In this work we investigate the change in the electrical properties (*I–V*) of Pt-, Ni- and Ti Schottky contacts on n-Ge (1 0 0) at different annealing temperatures in the temperature range 25–600 °C. Results presented here are based on the effects of thermal annealing on the current–voltage characteristics of the metal Schottky contacts at different annealing temperatures, which may be attributed to combined effects of interfacial reaction and phase transformation [17], during the annealing process.

2. Experimental procedures

To study the thermal annealing effects on the Schottky contacts, we used bulk-grown (1 0 0) oriented, n-type Ge, doped with antimony (Sb) to a density of $(2–3) \times 10^{15}\,cm^{-3}$ supplied by Umicore. Before metallization, the samples were first degreased and subsequently etched in a mixture of H_2O_2 (30%):H_2O (1:5) for 1 min. Immediately after cleaning they were inserted into a vacuum chamber where 120 nm of AuSb (0.6% Sb), was deposited by resistive evaporation on their back surfaces as ohmic contacts. The samples were then annealed at 350 °C in Ar for ten minutes to minimize the ohmic contact resistivity [18]. Before Schottky contact deposition, the samples were again chemically cleaned as described above. Ni Schottky contacts were resistively deposited under vacuum below 10^{-6} Torr, while Pt and Ti Schottky contacts were electron beam deposited. The contacts were 0.6 mm in diameter and 30 nm thick. The metal layer thickness and deposition rates were monitored with an INFICON XTC751-001-G1 quartz crystal thickness monitor. After contact fabrication, the samples were characterized by *I–V* measurements at room temperature to determine the quality of the diodes. The Schottky contacts were then isochronally annealed in an oven under Ar ambient in the temperature range 25–600 °C in steps of 25 °C for 30 min. *I–V* characteristic measurements followed each annealing cycle. Characterization of the films at different annealing temperatures was accomplished using a JEOL JSM-5800LV scanning electron microscopy (SEM) system operating at 5 kV.

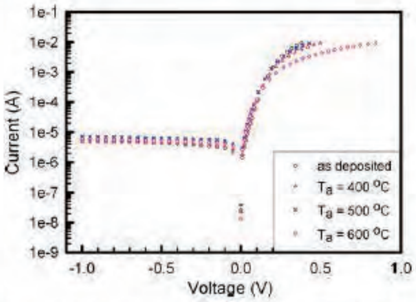

Fig. 1. Experimental forward and reverse *I–V* characteristics of one of the Pt/n-Ge (1 0 0) Schottky barrier diodes after isochronal thermal treatment for 30 min at different annealing temperatures: as-deposited, 400 °C, 500 °C and 600 °C.

3. Results and discussion

The barrier heights of the contacts were deduced from *I–V* characteristics, which were analyzed by the thermionic emission model given by the following equation [19,20]:

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

where

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

is the saturation current 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, n can be obtained from Eq. (1) as

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

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

We have fabricated eight Pt/-, Ni/- and Ti/n-Ge (1 0 0) Schottky barrier diodes (SBDs). Figs. 1–3 present the semilog forward and reverse bias *I–V* characteristics of these SBDs annealed in the 25–600 °C temperature range, together with those of as-deposited samples. The values of effective SBH were determined from the intercepts of the straight lines of the semilog-forward bias *I–V* characteristics with the help of Eq. (2). The effective SBHs and ideality

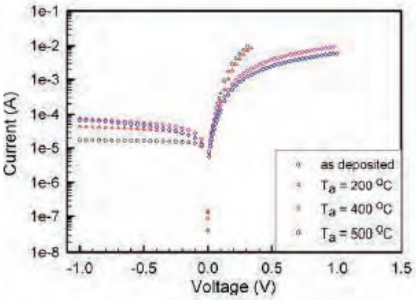

Fig. 2. Experimental forward and reverse *I–V* characteristics of one of the Ni/n-Ge (1 0 0) Schottky barrier diodes after isochronal thermal treatment for 30 min at different annealing temperatures: as-deposited, 200 °C, 400 °C and 500 °C.

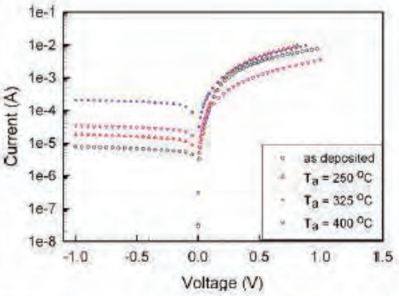

Fig. 3. Experimental forward and reverse *I–V* characteristics of one of the Ti/n-Ge (1 0 0) Schottky barrier diodes after isochronal thermal treatment for 30 min at different annealing temperatures: as-deposited, 250 °C, 325 °C and 400 °C.

factors vary from diode to diode; therefore it is common practice to take averages.

Fig. 4 shows the variation of the Schottky barrier height and reverse current at −1 V with annealing temperature for the Pt Schottky contacts. The SBH and reverse current at a bias voltage of −1 V for as-deposited Pt Schottky contacts were found to be (0.584 ± 0.005) eV and (5.46 ± 0.02) μA, respectively. The barrier height (BH) was approximately a constant within experimental error up to an annealing temperature of 350 °C. The BH then drops significantly, reaching (0.564 ± 0.005) eV after annealing at 500 °C. We suggest that there is a significant reaction between Pt and the Ge substrate. The change coincides with the initial phase formation of a germanide Ge_3Pt_2, which has been reported to form at 400 °C [1,4]. After annealing at 600 °C, the BH was found to increase to (577 ± 0.005) eV. The change in BH after the 500 °C anneal coincides with the temperature range of formation of a platinum germanide Ge_2Pt, reported by Grimaldi et al. [1] and Yao et al. [4] that forms after the 450 °C and 500 °C anneal, respectively. Throughout the annealing process the reverse current at −1 V remains in the same order of magnitude (10^{-5} to 10^{-6}) A.

Fig. 5 shows the variation of the Schottky barrier height and reverse current at −1 V with annealing temperature for the Ni Schottky contacts. The as-deposited SBH and reverse current at −1 V for Ni Schottky contacts were found to be (0.532 ± 0.005) eV and (29.20 ± 0.02) μA, respectively. The BH remains almost constant within experimental error in the tem-

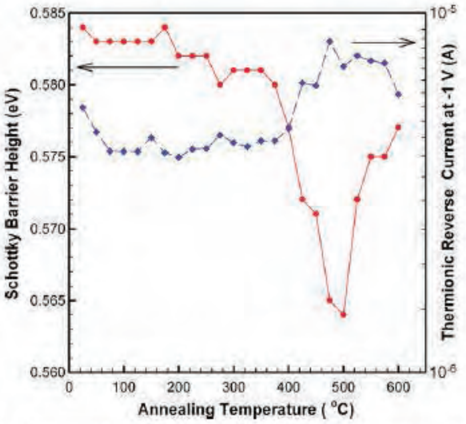

Fig. 4. Plot of the Schottky barrier height and the reverse current at −1 V as a function of annealing temperature for Pt Schottky contacts on n-Ge (1 0 0).

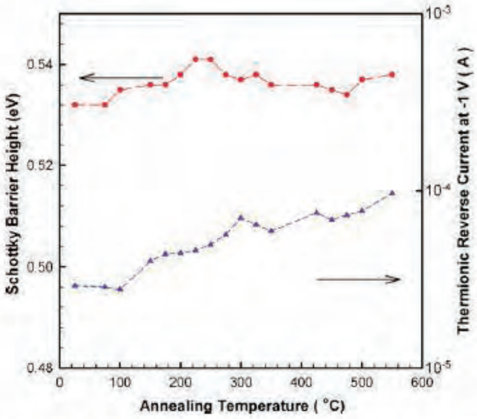

Fig. 5. Plot of the Schottky barrier height and the reverse current at −1 V as a function of annealing temperature for Ni Schottky contacts on n-Ge (1 0 0).

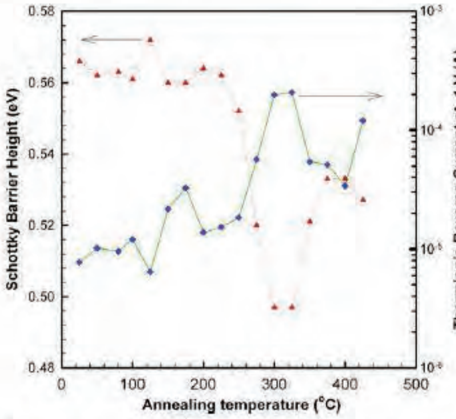

Fig. 6. Plot of the Schottky barrier height and the reverse current at −1 V as a function of annealing temperature for Ti Schottky contacts on n-Ge (1 0 0).

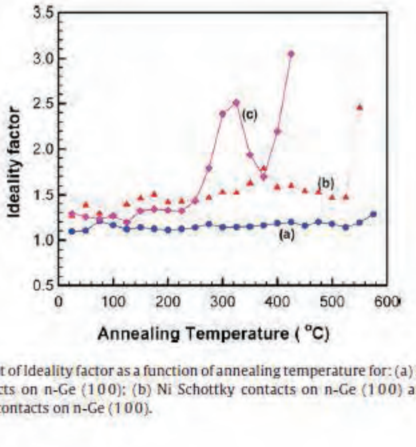

Fig. 7. Plot of Ideality factor as a function of annealing temperature for: (a) Pt Schottky contacts on n-Ge (1 0 0); (b) Ni Schottky contacts on n-Ge (1 0 0) and (c) Ti Schottky contacts on n-Ge (1 0 0).

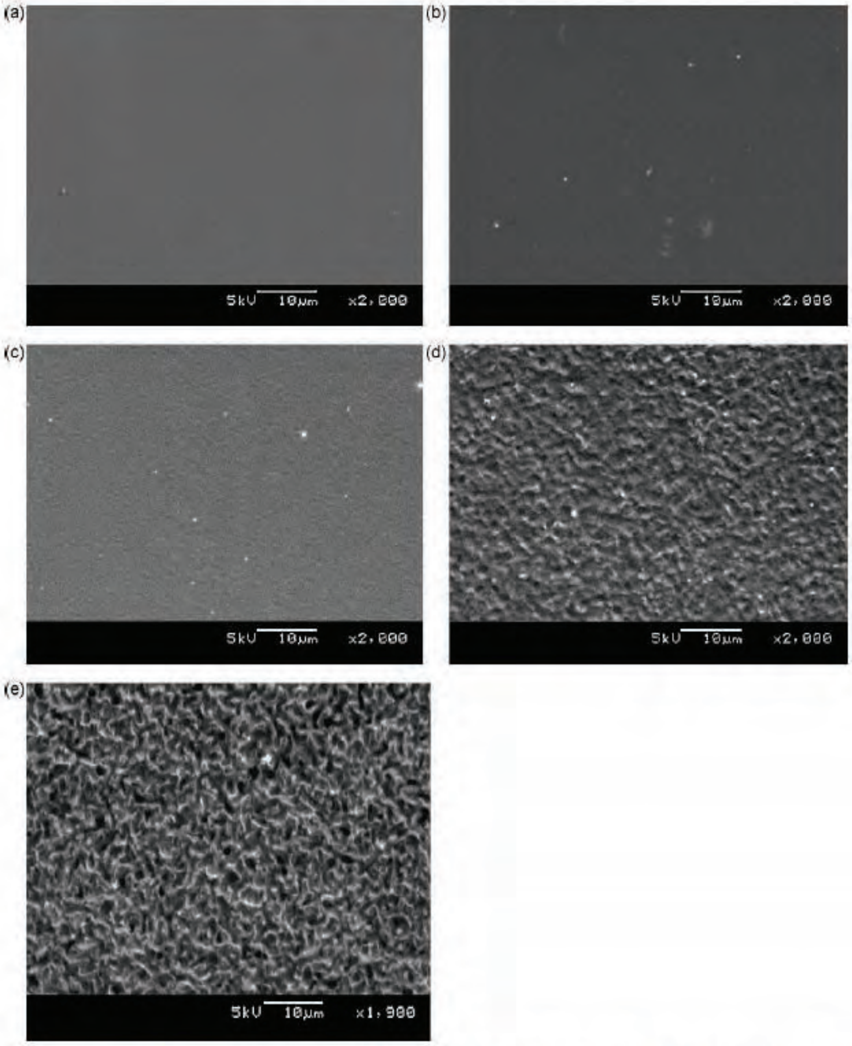

Fig. 8. SEM observation for Pt films deposited on germanium after isochronal thermal treat for 30 min at different annealing temperatures: (a) as-deposited, (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C.

perature range 100–525 °C. The near constant barrier height with annealing temperature in the Ni Schottky contacts may be attributed to the strong Fermi level pinning effect between Ni-germanide/n-Ge (1 0 0) substrates [16]. Studies by Gaudet et al. [5], Peng et al. [11] and An et al. [12] revealed the existence of only one germanide phase, NiGe for Ni in this temperature range.

The as-deposited SBH and reverse current at -1 V for Ti Schottky contacts were found to be (0.566 ± 0.005) eV and (7.76 ± 0.02) μA, respectively. Variation of barrier height and reverse current at a bias voltage of -1 V with annealing temperature for Ti Schottky contacts is shown in Fig. 6. The BH was approximately constant within experimental error up to an annealing temperature of 225 °C. After further annealing at higher temperatures the BH decreased, reaching a minimum value of (0.497 ± 0.005) eV at 300 °C. This change in BH could be associated with the phase formation of a germanide Ti_6Ge_5 which has been reported to form at 300 °C [16]. The subsequent increase in barrier height after annealing at temperatures higher than 300 °C coincides with the temperature range for the formation of the Ti_5Ge_3 germanide [16]. After a 425 °C anneal, *I–V* characteristics of the Ti Schottky contacts severely deteriorated, and the contacts became near-ohmic. Even after subjecting the Ti Schottky contacts to a temperature of 20 K, they showed no improvement in their rectifying behaviour.

It is well known that the interface states and chemical reactions between metals and semiconductors at interfaces can play an important role in the electrical properties of devices [17]. During the annealing process, metals may react with semiconductors and new compounds would form. Hence, the change of barrier heights may be attributed to the combined effects of interfacial reaction and phase transformation [17]. Furthermore, the barrier height change in Schottky contacts can be explained according to the effective work function (EWF) model [21], where the BH value is determined by the work function of microclusters of one or more phases resulting from either oxygen contamination or metal–semiconductor

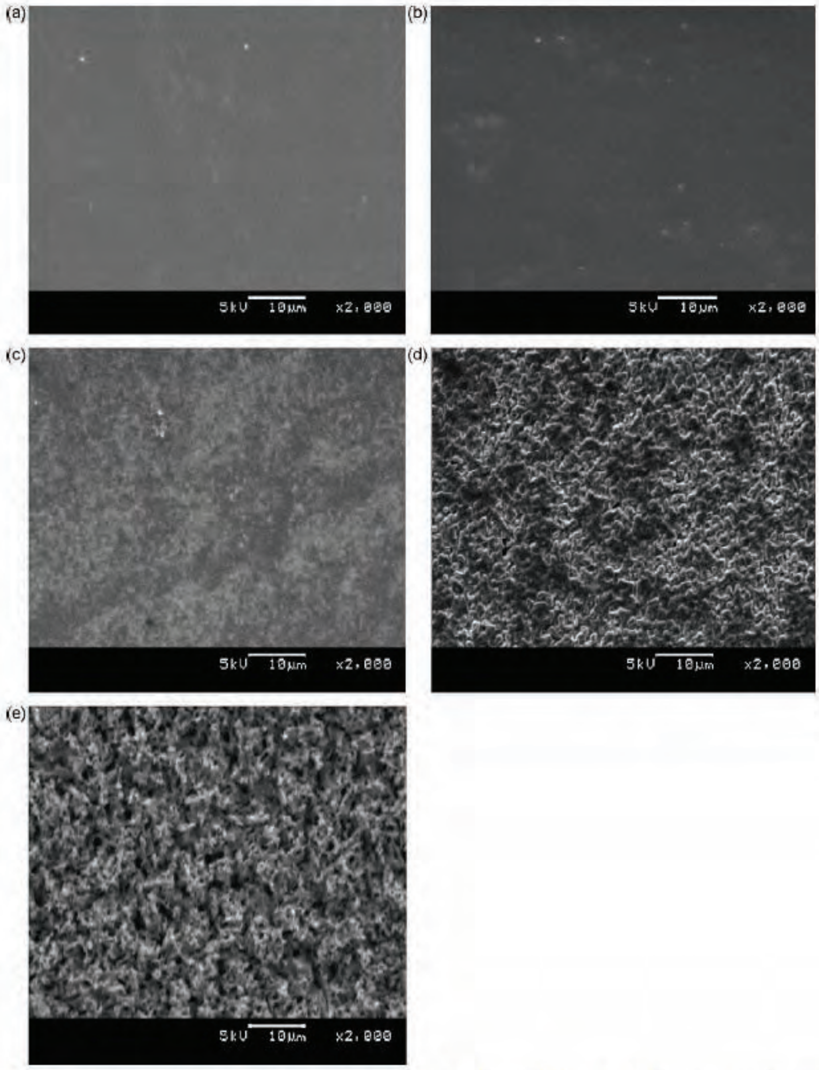

Fig. 9. SEM observation for Ni films deposited on germanium after isochronal thermal treat for 30 min at different annealing temperatures: (a) as-deposited, (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C.

reactions which occur during metallization and annealing, and each phase having its own effective work function [22].

The ideality factor was calculated from the gradient of the linear region of the experimental ln *I*–*V* characteristics in forward bias [2]. The variation of the Pt Schottky contacts ideality factor is shown in Fig. 7(a). The ideality factor was found to be between 1.09 and 1.30. Fig. 7(a) shows that the ideality factor is almost constant, 1.09 up to a temperature of 575 °C. It then increases to 1.30 after annealing at 600 °C.

Fig. 7(b) shows the variation of ideality factor with annealing temperature for the Ni Schottky contacts. The ideality factors were between 1.27 and 1.47 at annealing temperatures between 25 °C and 525 °C. The variation of ideality factor with annealing temperature for Ti Schottky contacts is shown in Fig. 7(c). The ideality factors were between 1.29 and 3.05 at annealing temperatures between 25 °C and 425 °C. In the case of Ni and Ti Schottky contacts, ideality factors significantly greater than 1.0 indicate that the transport properties are not well modeled by thermionic emission alone although their contacts remain rectifying [23]. Therefore, the SBH is merely a curve fitting parameter for these contacts and is not representing the true BH. The non-idealities are mostly due to the states associated with the defects near the surface of the semiconductor [2]. In a Schottky contact, even with a good surface treatment, there is an interfacial oxide layer of thickness about 1 nm with a considerable amount of surface states [2]. Interface states, inter-diffusion, chemical reaction, compound formation, defects generation, etc. can all be derived from thermodynamics due to thermal annealing [24–26]. These may lead to recombination centres [23] and SBH

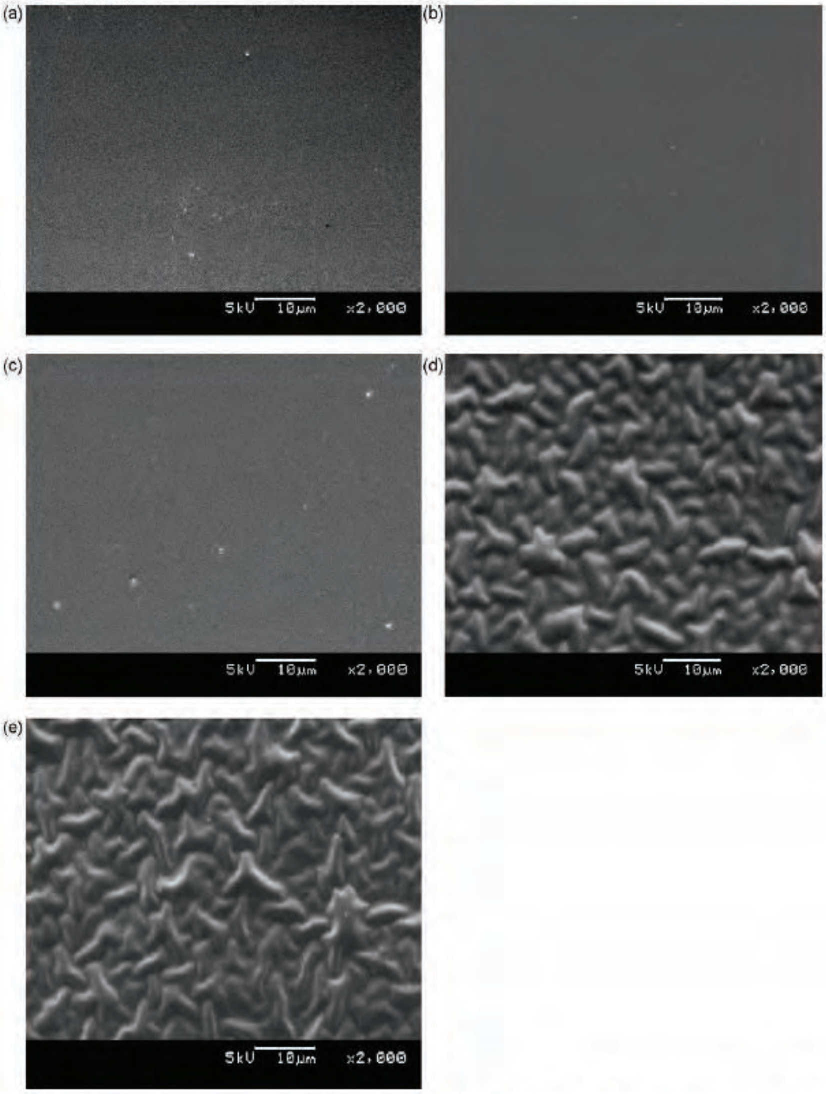

Fig. 10. SEM observation for Ti films deposited on germanium after isochronal thermal treat for 30 min at different annealing temperatures: (a) as-deposited, (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C.

inhomogeneities [27], which cause a flow of excess current leading to a deviation from the ideal thermionic emission behaviour at low voltages and temperatures.

Scanning electron microscopy (SEM) observations were conducted for Pt-, Ni- and Ti/n-Ge (1 0 0) samples, as-deposited and annealed at different temperatures. Results are shown in Figs. 8–10. The morphological evolution of Pt/n-Ge (1 0 0) is shown in Fig. 8. As seen in Fig. 8(a), (b) and (c), metal surfaces show little change when samples were annealed below 600 °C. This is in agreement with what was reported by Yao et al. [4]. The Pt-germanide exhibited no sign of agglomeration even up to 500 °C anneal, suggesting better morphological stability for Pt-germanide films [4]. At 600 °C, anneal and above (see Fig. 8(d–e)), the surface becomes rough, indicating the agglomeration of Pt, finally destroying the contact, as evidenced by the loss of rectifying properties of the Pt Schottky contacts after 625 °C anneal. From the results, it can be concluded that the onset temperature in the 30-nm Pt/Ge (1 0 0) system occurs at 600–700 °C.

Fig. 9 shows the evolution of surface morphology for Ni/n-Ge (1 0 0) with annealing temperatures. Although Zhang et al. [28] and Lee et al. [29] have reported grain growth and groove deepening at the surface at 400 °C for Ni film thickness of 15 nm, with Yao et al. [4] reporting the development of severe grain boundary grooving after 500 °C anneal (onset temperature for 15 nm Ni film agglomeration), prominent grain growth at the surface (see Fig. 9(c)) were evident up to 500 °C, indicating inception of agglomeration. Agglomeration starts with grain boundary grooving and progresses to island formation [29]. After a 600 °C anneal, we observed development of severe grain grooving. The temperature at which grain growth and agglomeration occurs decreases with reduced film thickness [28]. This is consistent with the grooving model for agglomeration [28], as in our study the metal film thickness was 30 nm. We also observed that after 700 °C (see Fig. 9 (e)), film continuity was severely interrupted as indicated by the dark spots caused by exposed Ge regions. The agglomeration is driven by the minimization of the total surface/interface energy of the metal-germanide and germanium substrate [30]. We found the onset of the agglomeration process for 30 nm Ni/Ge (1 0 0) system to be in 500–600 °C.

Fig. 10 shows the SEM images of Ti/n-Ge (1 0 0) films at different annealing temperatures. Although Ti/Schottky contacts lost their rectifying behaviour after 425 °C anneal, the metal surface shows no change when the sample was annealed below 600 °C. Grain growth and grove deepening at the surface were evident up to 700 °C, suggesting better morphological stability.

4. Conclusions

Ni Schottky contacts were fabricated by resistive deposition. Pt and Ti Schottky contacts were fabricated by electron beam deposition. The Schottky contacts behaviour was investigated under various annealing conditions. SEM observations were conducted for samples annealed at different temperatures. The variation of Schottky barrier heights and ideality factors with annealing temperature may be attributed to interfacial reactions of metals (Pt, Ni, Ti) with germanium and the phase transformation of the metal-germanides during annealing. Ni and Ti show initial stages of reaction with Ge after annealing at 100 °C and 225 °C, respectively. The electrical properties of the metal Schottky contacts reveal that Pt Schottky contacts are of high quality with low reverse currents at −1 V of the order (10^{-5} to 10^{-6}) A and ideality factors as low as 1.09. The as-deposited BHs near the bandgap of Ge in the Pt/-, Ni/- and Ti/n-Ge (1 0 0) Schottky contacts imply good Schottky source/drain contact materials in p-channel Ge-MOSFETS, for the hole injection from source into inverted p-channel [4]. From SEM observations, it can be concluded that the onset temperature in 30 nm Ni- and Pt/n-Ge (1 0 0) systems occurs at 500–600 °C and 600–700 °C, respectively.

Acknowledgements

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References

[1] M.G. Grimaldi, L. Wieluński, M.-A. Nicolet, Thin Solid Films 81 (1981) 207.
[2] A.R. Saha, S. Chattopadhyay, C.K. Maiti, Mater. Sci. Eng. B 114–115 (2004) 218.
[3] R. Li, H.B. Yao, S.J. Lee, D.Z. Chi, M.B. Yu, G.Q. Lo, D.L. Kwong, Thin Solid Films 504 (2006) 28.
[4] H.B. Yao, C.C. Tan, S.L. Liew, C.T. Chua, C.K. Chua, R. Li, R.T.P. Lee, S.J. Lee, D.Z. Chi, International Workshop on Junction Technology Proceeding, 2006, p. 164.
[5] S. Gaudet, C. Detavernier, A.J. Kellock, P. Desjardins, C. Lavoie, J. Vac. Sci. Technol. A 24 (3) (2006) 474.
[6] R. Gumeniuk, W. Schnelle, H. Rosner, M. Nicklas, A. Leithe-Jasper, Yu Grin, Phys. Rev. Lett. 100 (2008) 0170021.
[7] A. Łaszcz, J. Ratajczak, A. Czerwinski, J. Kątcki, V. Srot, F. Phillipp, P.A. van Aken, N. Breil, G. Larrieu, E. Dubois, Mater. Sci. Eng. B 154–155 (2008) 175.
[8] F. Ohtsu, H. Fukuoka, S. Yamanaka, J. Alloys Compd. (2009), doi:10.1016/j.jallcom.2009.08.052.
[9] A. Thanaillakis, D.C. Northrop, Solid State Electron. 16 (1973) 1383.
[10] F. Nemouchi, D. Mangelinck, J.L. Lábár, M. Putero, C. Bergman, P. Gas, Microelectron. Eng 83 (2006) 2101.
[11] C.-Y. Peng, Y.-H. Yang, C.-M. Lin, Y.-J. Yang, C.-F. Huang, C.W. Liu, International Conference on Solid-State and Integrated Circuits Technology Proceedings (ICSICT), art. no. 4734645 (2008) 681.
[12] X. An, C. Fan, R. Huang, X. Zhang, Proceedings – Electrochemical Society, PV 1, 2008, p. 406.
[13] C.-Y. Peng, C.-F. Huang, Y.-J. Yang, C.W. Liu, ECS Trans. 16 (2008) 249.
[14] X. An, C. Fan, R. Huang, X. Zhang, Chin. Phys. Lett. 26 (2009) 0873041.
[15] C. Perrin, D. Mangelinck, F. Nemouchi, J. Labar, C. Lavoie, C. Bergman, P. Gas, Mater. Sci. Eng. B 154–155 (2008) 163.
[16] Dedong Han, Xin Wang, Yi Wang, Dayu Tian, Wei Wang, Xiaoyan Liu, Jinfeng Kang, Ruqi Han, Microelectron. Eng. 82 (2005) 93.
[17] Y. Sun, X.M. Shen, J. Wang, D.G. Zhao, G. Feng, Y. Fu, S.M. Zhang, Z.H. Zhang, Z.H. Feng, Y.X. Bai, H. Yang, J. Phys. D: Appl. Phys. 35 (2002) 2648.
[18] F.D. Auret, P.J. Janse van Rensburg, M. Hayes, J.M. Nel, S. Coelho, W.E. Meyer, S. Decoster, V. Matias, A. Vantomme, D. Smeets, Nucl. Instrum. Methpds B 257 (2007) 169.
[19] S.M. Sze, Physics of Semiconductor Devices, New York, 1981, p. 245.
[20] Baojun Li, Soo-Jin Chua, Yakovlev Nikolai, Lianshan Wang, Eng-Kee Sia, Solid State Electron. 47 (2003) 602.
[21] J.L. Freeouf, J.M. Woodall, Appl. Phys. Lett. 29 (1976) 263.
[22] E. Ayyıldız, A. Türüt, Solid State Electron. 43 (1999) 521.
[23] H. Doğan, N. Yıldırım, A. Turut, Microelectron. Eng. 85 (2008) 655.
[24] T. Sands, Appl. Phys. Lett. 52 (1988) 197.
[25] S.K. Cheung, N.W. Cheung, Appl. Phys. Lett. 49 (1986) 85.
[26] J.L. Everaet, R.L. Van Meirhaeghe, W.H. Laflére, F. Cardon, Semicond. Sci. Technol. 5 (1990) 60.
[27] R.T. Tung, J.P. Sullivan, F. Schrey, Mater. Sci. Eng. B 14 (1992) 266.
[28] Q. Zhang, N.W. Wu, T. Osipowicz, L.K. Bera, C. Zhu, Jpn. J. Appl. Phys. 44 (2005) L1389.
[29] K.Y. Lee, S.L. Liew, S.J. Chua, D.Z. Chi, H.P. Sun, X.Q. Pan, Mater. Res. Symp. 810 (2004) 55.
[30] J.P. Gambino, E.G. Colgan, Mater. Chem. Phys. 52 (1998) 99.

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Comparison of metal Schottky contacts on n-Ge (100) at different annealing temperatures

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Platinum (Pt), nickel (Ni), palladium (Pd) and cobalt (Co) Schottky barrier diodes were fabricated by vacuum resistive evaporation or electron beam deposition. We have studied the electrical characteristics of platinum, nickel, palladium and cobalt Schottky contacts on bulk grown (100) Sb-doped n-type germanium under various annealing conditions by current – voltage (*I-V*) measurements. The Schottky behaviour of the metal contacts with annealing temperatures is compared. Results obtained from the electrical properties of the Schottky contacts have revealed that Pt contacts are highly thermally stable over a wide range of temperature compared to Pd, Ni and Co contacts. Furthermore, Pt Schottky contacts are of highest quality, with low reverse currents of the order (10^{-6}- 10^{-5} A) and as-deposited ideality factor as low as 1.09, compared to Pd, Ni, and Co Schottky contacts.

1 Introduction Thin film reactions of metal on semiconductor have been of interest for the past 30 years for their applications in microelectronic devices [1]. In the manufacturing of semiconductor devices, metal contacts have always played a pivotal role, especially in MOSFET and CMOS devices. A good metal-semiconductor (MS) contact is essential for the successful operation of the electronic circuits and devices [2]. Contacts to very large scale integration (VLSI) circuits require MS contacts, which are thermally stable, have low resistivity and are compatible with the process technology. Schottky contacts play an important role in controlling the electrical performances of semiconductor devices [2]. The attempts to develop faster devices in modern microelectronics have increased the interest for alternative materials to silicon, compatible with the existing silicon-based technology [3]. Germanium (Ge) has been regarded as the replacement for silicon due to its high carrier mobility, low effective mass of holes [4] and relative compatibility with silicon processing. This has led to renewed interest in the complete understanding of metal-germanium interactions and electronic properties of radiation and process-induced defects in Ge.

The reactions of germanium with Pt[5 , 6 , 7], Ni [8,9,10,11,12], Pd [6,9,13,14,15] and Co [9,13,16,17] have also been investigated previously. Study of the solid state reaction between the metal films and germanium to determine the phase formation sequence [5,9,11,13,15,17], microstructure of material [9,10,12], growth kinetics[11,16] and electrical characteristics [9,10,12],were analyzed by x-ray diffraction, Rutherford backscattering spectroscopy, transmission electron microscopy, differential calorimetry and current-voltage (*I-V*) techniques respectively. Thanailakis *et al.* [8] established a relationship between as-deposited Pd/n-Ge (111) and Ni/n-Ge (111) Schottky barrier height values, the metal work functions and the density of surface states of germanium substrate. Yao *et al.* [10] studied the *I-V* characteristics of Pt/n-Ge (001) and Ni/n-Ge (001) after subjecting the Schottky contacts to rapid thermal anneal (RTA) in N_2 ambient in the temperature range 250-700 °C for 20 s. Han *et al.* [12] has reported the changes in the electrical properties of Ni germanide Schottky contacts on n-Ge (100) in the temperature range 300-500 °C.

The aim of this paper is to report the change in the electrical properties and give a comparative study of thermal stability of the Pt, Ni, Pd and Co Schottky contacts on n-Ge (100), in the temperature range 25-600 °C. Results presented here are based on the thermal annealing effects on the *I-V* characteristics of the Pt, Ni, Pd and Co Schottky contacts, which may be attributed to combined effects of interfacial reaction and phase transition [18], during the annealing process.

2 Experimental procedures

Bulk-grown, (100) oriented, n-type Ge samples, doped with antimony, (Sb) to a density of (2-3) x 10^{15} cm^{-3} supplied by Umicore, were degreased in successive trichloroethylene, acetone and methanol ultrasonic baths and subsequently etched in a mixture of H_2O_2 30%: H_2O (1:5) for 1 minute. Immediately after cleaning they were inserted into a vacuum chamber where AuSb (0.6% Sb), 120 nm thick, was deposited by resistive evaporation on their back surfaces as ohmic contacts. The samples were then annealed at 350 °C in Ar for 10 minutes to minimize the contact resistivity of the ohmic contacts [19]. Before Schottky contact deposition, the samples were again chemically cleaned as described above. Ni and Pd Schottky contacts were deposited by vacuum resistive evaporation and the Pt and Co Schottky contacts were deposited by electron beam deposition. The vacuum was maintained at below 1×10^{-6} Torr during the depositions. These Schottky contacts were deposited through a mechanical mask resulting in an array of 0.6 mm diameter contacts. After the contacts fabrication the samples were characterized by current-voltage (*I-V*) measurements at room temperature to determine the quality of the diodes. The Schottky contacts were then isochronally annealed in an oven under Ar gas from 25 °C to 600 °C in steps of 25 °C for 30 min. *I-V* measurements followed each annealing cycle.

3 Results and discussion

The *I-V* characteristics are widely used to study the performance of the Schottky contacts since they offer many important device parameters. The barrier heights of the contacts were deduced from *I-V* characteristics which were analyzed by using the thermionic emission model given by the following equation [20,21]:

$$I(V) = A^{*}AT^{2}\exp(-q\Phi_{B}/kT)[\exp(qV/nkT)-1] \qquad (1)$$

where A^* is the effective Richardson constant, A is the diode cross-sectional area, T the measurement temperature, k the Boltzmann constant, Φ_B the Schottky barrier height (SBH), and n the ideality factor which can be determined accurately from the linear part of the forward bias ln I versus V plot, and assuming pure thermionic emission can be obtained as:

$$n=\frac{q}{kT}\frac{dV}{d(\ln(I))} \qquad (2)$$

The SBH values were determined using the intercepts of the straight lines of semi log-forward bias *I-V* characteristics with help of equation

$$\Phi_{B}=\frac{kT}{q}\ln\left(\frac{A^{*}AT^{2}}{I_{0}}\right) \qquad (3)$$

Table 1 Electrical parameters for as-deposited Pt, Pd, Ni and Co Schottky contacts on n-Ge (100).

metal	Work function (eV)[a]	SBH (eV)	Ideality factor	Reverse current density at –1V(A/cm^2)
Pt	5.65	0.584±0.005	1.09±0.02	1.93 x 10^{-3}
Pd	5.12	0.540±0.005	1.15±0.02	6.00 x 10^{-3}
Ni	5.15	0.532±0.005	1.27±0.02	10.30 x 10^{-3}
Co	5.00	0.513±0.005	1.41±0.02	32.4 x 10^{-3}

[a] Ref. [22,23,24,25],which give the currently accepted values of the work functions for the metals, Pt, Pd, Ni and Co.

Figure 1 shows a linear correlation of the as-deposited SBH values and work functions for the metals Pt, Pd, Ni and Co, cornfirming the Effective Work Function model.

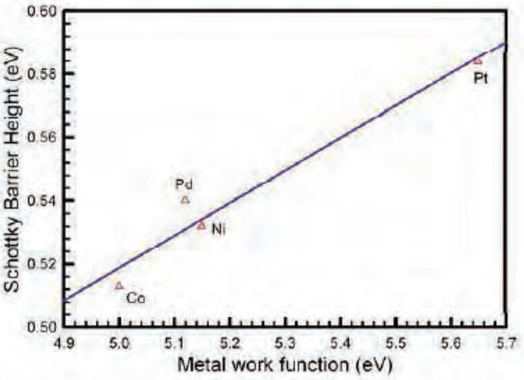

Figure 1 Plot of the as-deposited Schottky barrier heights against published values of metals Pt, Pd, Ni and Co work function.

From Table 1 we see that the as-deposited electrical parameters for Pt and Pd Schottky contacts reveal relatively better quality compared to the Schottky contacts of Ni and Co. It has been shown that the electrical properties and stability of semiconductor devices are strongly influenced by contaminants inadvertently introduced during the many processing steps involved during device fabrication [26]. It is also known that the interface states and chemical reactions between metals and semiconductors at interface also play an important role in the electrical properties of devices.

Figure 2 shows the variation of the Schottky barrier height with annealing temperature. The as-deposited Pt Schottky contacts barrier height is the highest due to the fact that its work function (Table 1) is significantly higher than that of other metals investigated here. Although four Pt germanide phases are reported to form during annealing between 25-600 °C [5], Fig. 2 and Fig. 3 depict that Pt contact electrical parameters are approximately constant up to 350 °C. The change coincides with the initial phase formation of a germanide Ge_3Pt_2, reported by Grimaldi *et al.* [5] and Yao *et al.* [10] to form at an annealing temperature of 400 °C. The Pt SBH then increases to 0.578 ± 0.005 eV after annealing the sample at a temperature of 600 °C. The SBH change after a 500 °C anneal coincides with the temperature range of formation of a platinum germanide Ge_2Pt, reported to form after a 450 °C anneal [5,9,10].

The variation in the electrical parameters of Co Schottky contacts (Fig. 2 and Fig. 3) coincide with the temperature ranges of Co germanide phases formed by annealing as reported by Hsieh *et al.* [7] and Sun *et al.* [27], CoGe forming between 100-300 °C, Co_5Ge_7 forming around 300 °C and $CoGe_2$ forming at temperatures above 425 °C. The variation of Ni and Pd Schottky contacts barrier height between 100-525 °C annealing temperatures is approximately constant within experimental error of ±5 %. According to Gaudet *et al* [9], only one germanide phase exists for both Ni (NiGe) and Pd (PdGe) in this temperature range.

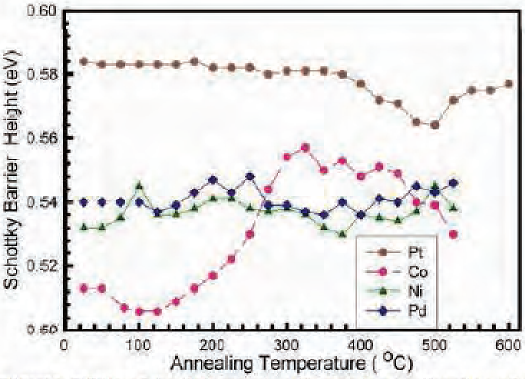

Figure 2 Plot of the Schottky barrier height as a function of annealing temperature for Co, Ni, Pd and Pt Schottky contacts on n-Ge (100).

During the annealing process, metals may react with germanium, forming new compounds. The change of barrier heights may be attributed to the combined effects of interfacial reaction and phase transition [18]. The SBH is also temperature dependent, due to the fact that the measured current across a Schottky junction is a combination of thermionic emission and recombination currents [2]. Furthermore, the barrier height change in Schottky contacts can be explained according to the effective work function (EWF) model [28], where the value of barrier height is determined by the work function of microclusturs of one or more phases resulting from either oxygen contamination or metal-semiconductor reactions which would occur during metallization and annealing, each phase having its own effective work function [29].

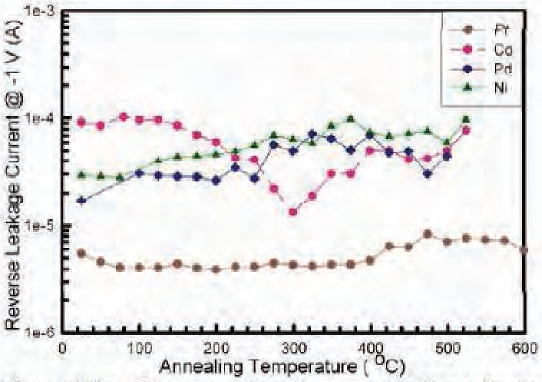

Figure 3 Plot of the reverse leakage current at -1 V as a function of annealing temperature for Pt, Pd, Ni and Co Schottky contacts on n-Ge (100).

Figure 3 shows the variation of reverse leakage current at -1 V with annealing temperature for the Pt, Pd, Ni and Co Schottky contacts. Throughout annealing process the reverse leakage current at -1 V for Pt Schottky contacts was the lowest, in the range (10^{-6}-10^{-5}) A. The variation of the Pt electrical properties during the annealing process reveal that, Pt Schottky contacts are highly thermally stable over a wide range of temperature, as after 525 °C anneal the Pd, Ni and Co Schottky contacts lost their rectifying behaviour.

The ideality factor was calculated from the gradient of the linear region of the experimental ln (*I*) - *V* characteristics in forward bias [2]. The variation of the Pt, Ni, Pd and Co Schottky contacts ideality factor with annealing temperature is shown in Fig. 4. The Pt Schottky contacts ideality factor was found to be between 1.09 and 1.19, in the temperature range 25-550 °C. It then increased after 575 °C anneal. The ideality factors for Ni, Pd and Co are found to be greater than 1.1, indicating that the transport properties are not well modeled by thermionic emission alone although their contacts remain rectifying [30]. The deviation from ideality is mostly due to the states associated with the defects near surface of the semiconductor [2]. These interface states, and inter-diffusion, chemical reaction, compound formation, defects generation, etc. can all be derived by thermodynamics due to thermal annealing [31,32,33], may lead to recombination centers [30] and Schottky barrier inhomogeneities [34], giving rise to excess current, which causes deviation from the ideal thermionic emission behaviour at low voltages and temperature.

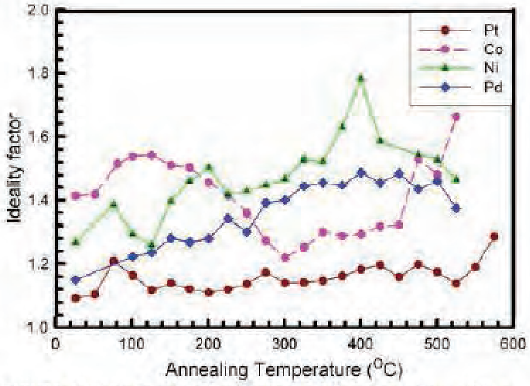

Figure 4 Plot of the Ideality factor as a function of annealing temperature for Pt, Pd, Ni and Co Schottky contacts on n-Ge (100).

4 Summary Ni and Pd Schottky contacts were fabricated by resistive deposition. Pt and Co Schottky contacts were fabricated by electron beam deposition. These Schottky contacts electrical properties were investigated under various annealing conditions and results compared. The variation of barrier heights and ideality factors with different annealing temperatures may be attributed to interfacial reactions of metals (Pt, Ni, Pd and Co) with germanium and phase transition of the metal-germanides during annealing. The results show that Pt Schottky contacts are highly thermally stable over a wide range of temperature compared to the Ni, Co and Pd Schottky contacts, and Pt Schottky contacts have best quality with lowest reverse leakage currents of the order (10^{-5}-10^{-6}) and as deposited ideality factors as low as 1.09.

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References

[1] F. Nemouch, D. Mangelinck, J.L LáBár, M. Putero, C. Bergma, and P. Gas, Microelectron. Eng. **83**, 2101-2106 (2006).
[2] A.R. Saha, S. Chattopadhyay, C.K. Maiti, Mater. Sci. Eng. B **114/115**, 218 (2004).
[3] V.I. Kolkovsky, M. C. Petersen, and A. N. Larsen, Appl. Phys. Lett. **90**, 112110 (2006).
[4] R. Hull and J. C. Bean (Eds.), Germanium Silicon: Physics and Materials, Semiconductors and Semi-metals, Vol. 56 (Academic, San Diego, 1999).
[5] M.G. Grimaldi, L. Weiluński, and M. A. Nicolet, Thin Solid Films **81**, 207 (1981).
[6] E.D. Marshall, C.S. Wu, C.S. Pai, D.M. Scott, and S.S. Lau, Thin Films: The Relationship of Structure to Properties, MRS Symposia Proceeding (Material Research Society, Pittsburg, PA, 1985), pp. 161-166.
[7] Y.F. Hsieh and L.J. Chen, J. Appl. Phys. **63**, 1177 (1988).
[8] A. Thanailakis and D.C. Nortrop, Solid-State Electron. **16**, 1383 (1973).
[9] S. Gaudet et al., J. Vac. Sci. Technol. A **24**(3), 474 (2006).
[10] H.B. Yao, C.C. Tan, S.L. Liew, C.T. Chua, C.K. Chua, R. Li, R.T.P. Lee, S.J. Lee, and D.Z. Chi, Proc. International Workshop on Junction Technology (2006), p. 164.
[11] F. Nemouchi, D. Mangelinck, J.L. Lábár, M. Petero, C. Bergman, and P. Gas, Microelectron. Eng. **83**, 2101 (2006).
[12] D. Han, X. Wang, Y. Wang, D. Tian, W. Wang, X. Liu, J. Kang, and R. Han, Microelectron. Eng. **82**, 93 (2005).
[13] M. Wittmer, M.A. Nicolet, and J.W. Mayer, Thin Solid Films **42**, 51 (1977).
[14] G. Ottaviani, C. Canali, G. Ferrari, G. Majni, M. Prudenziati, and S.S. Lau, Thin Solid Films **47**, 187 (1977).
[15] Y.F. Hsieh and L.J. Chen, Thin Solid Films **162**, 295 (1988).
[16] Y.F. Hsieh, L.J. Chen, L.J. Marshall, and S.S. Lau, Appl. Phys. Lett. **51**, 1588 (1987).
[17] S.P. Ashburn, M.C. Öztürk, G. Harris, and D.M. Maher, J. Appl. Phys. **74**, 4455 (1993).
[18] Y. Sun, X.M. Shen, J.Wang, D.G. Zhao, G.Feng, Y.Fu, S.M. Zhang, Z.H. Zhang, Z.H. Feng, Y.X. Bai, and H. Yang, J.Phys. D: Appl. Phys. **35**, 2648 (2002).
[19] http://ece-www.colorado.edu/bart/book/surfstart.htm.
[20] S.M. Sze, Physics of Semiconductor Devices (New York, 1981), p. 245.
[21] Baojun Li, Soo-Jin Chua, N. Yakovlev, Lianshan Wang, and Eng-Kee Sia, Solid-State Electron. **47**, 601 (2003).
[22] http://environmentalchemistry.com/yogi/periodic/Pt.html (12.10.2009)
[23] http://environmentalchemistry.com/yogi/periodic/Pd.html (12.08.2009)
[24] http://environmentalchemistry.com/yogi/periodic/Ni.html (12.10.2009)
[25] http://environmentalchemistry.com/yogi/periodic/Co.html (12.10.2009)
[26] B. Şahin, H. Çetin, and E. Ayyildiz, Solid State Commun. **135**, 490 (2005).
[27] H. P. Sun, Y.B. Chen, X. Q. Pan, D.Z. Chi, R. Nath, and Y. L. Foo, Appl. Phys. Lett. **86**, 071904 (2005).
[28] J. L. Freeouf and J.M. Woodall, Appl. Phys. Lett. **29**, 263 (1976).
[29] E.Ayyilidz and A.Türüt, Solid-State Electron. **43**, 521 (1999).
[30] H. Doğan, N. Yildirim, A. Türüt, Microelectron. Eng. **85**, 655 (2008).
[31] T. Sands, Appl. Phys. Lett. **52**, 197 (1988).
[32] S.K. Cheung and N.W. Cheung, Appl. Phys. **49**, 85 (1986).
[33] J.L. Everaet, R.L. Van Meirhaeghe, W.H. Laflére, and F. Cardon, Semicond. Sci. Technol. **5**, 60 (1990).
[34] R.T. Tung, J.P. Sullivan, and F. Schrey, Mater. Sci. B **14**, 266 (1992).