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Electrical characterisation of ruthenium Schottky contacts on *n*-Ge (1 0 0)

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ABSTRACT

Ruthenium (Ru) Schottky contacts were fabricated on *n*-Ge (1 0 0) by electron beam deposition. Current–voltage (*I*–*V*), deep level transient spectroscopy (DLTS), and Laplace-DLTS techniques were used to characterise the as-deposited and annealed Ru/*n*-Ge (1 0 0) Schottky contacts. The variation of the electrical properties of the Ru samples annealed between 25 °C and 575 °C indicates the formation of two phases of ruthenium germanide. After Ru Schottky contacts fabrication, an electron trap at 0.38 eV below the conduction band with capture cross section of $1.0\times10^{-14}\,cm^{-2}$ is the only detectable electron trap. The hole traps at 0.09, 0.15, 0.27 and 0.30 eV above the valence band with capture cross sections of $7.8\times10^{-13}\,cm^{-2}$, $7.1\times10^{-13}\,cm^{-2}$, $2.4\times10^{-13}\,cm^{-2}$ and $6.2\times10^{-13}\,cm^{-2}$, respectively, were observed in the as-deposited Ru Schottky contacts. The hole trap H(0.30) is the prominent single acceptor level of the E-centre, and H(0.09) is the third charge state of the E-centre. H(0.27) shows some reverse annealing and reaches a maximum concentration at 225 °C and anneals out after 350 °C. This trap is strongly believed to be V–Sb_2 complex formed from the annealing of V–Sb defect centre.

1. Introduction

The metal–semiconductor (MS) structures are of important applications in electronics industry [1]. The applications consist of microwave field effect transistors, phototransistors, quantum confinement devices, radio-frequency detectors, heterojunction bipolar transistors and space solar cell [2–4]. A good MS contact is essential for the successful operation of these electronic devices. Schottky contacts play an important role in controlling the electrical performances of semiconductor devices and Schottky barrier height (SBH) [5], which is an important parameter that determines the electrical characteristics of the MS contacts [6]. 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 [7]. The aggressive shrinking of advanced complementary metal-oxide semiconductor (CMOS) device feature size results in the requirements for new materials and device structures to relax the physical limitation in device scaling [8]. The high carrier mobility [9], low effective mass of holes [10] and relative compatibility with silicon processing have made germanium (Ge) a potential alternative to silicon. 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 because defects ultimately determine the performance of devices fabricated thereon [10]. These defects influence device performance and alter the barrier heights (BHs) of the contacts [11]. The defects responsible for these BH adjustments are introduced when energetic particles impinge on the semiconductor surface during device processing or during device operation in radiation environment. Depending on the application, these defects may either be detrimental or beneficial for optimum device operation. A lot of research work has been performed on the electrical properties of defects introduced during high-energy, electron and proton irradiation of Ge [12–17]. The defects introduced during the electron beam deposition of platinum (Pt) Schottky contacts on *n*-Ge and the electronic properties of defects introduced during the implantation of Ge with heavier ions, such as dopants have also been reported [18]. Metallisation is a critical processing step in the semiconductor industry. Electron beam deposition (EBD), sputter deposition and resistive evaporation are commonly used metallisation methods. EBD or Sputter deposition are known to introduce defects on and below the semiconductor surfaces. Defects introduced in Ge during metallisation processes have been investigated [19–21].

In this study we report the change in the electrical properties of ruthenium (Ru) Schottky contacts on *n*-Ge (1 0 0) at different

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furnace annealing temperatures in the temperature range 25–575 °C, and the electronic properties of defects introduced in n-Ge (1 0 0) during electron beam deposition (EBD) of Ru Schottky contacts and annealing process. A practical concern is whether the germanidation process introduces defects, because this may affect the leakage current of the source–drain junctions. Results presented here are based on the effects of the thermal treatment on the I–V characteristics of Ru Schottky contacts at different isochronal annealing temperatures in the temperature range 25–575 °C, which may be due to the combined effects of phase transformation and interfacial reactions.

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} and supplied by Umicore. Before metallisation 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, the samples were inserted into a vacuum chamber where AuSb (0.6% Sb), 100 nm thick, was deposited by resistive evaporation as the back ohmic contacts. A 10 min annealling at 350 °C in argon (Ar) to lower the barrier height and increase the ohmic behaviour of the contact was performed. Before the Schottky contact deposition, the samples were again chemically cleaned as described above. Ru contacts were deposited using an EBD system through a mechanical mask. These contacts were deposited under vacuum with a pressure below 10^{-6} Torr. The contacts were (0.60 ± 0.05) mm in diameter and 30 nm thick. The thickness of the contacts and the deposition rate were monitored using an INFICON XTC 751-001-G1 quart crystal thickness monitor. After the contact fabrication, the samples were characterised using the current–voltage (I–V) measurements at room temperature to determine the quality of the diodes. The electrical characterisation was repeated after every annealing cycle in Ar gas for 30 min between 25 °C and 575 °C. The defects introduced were characterised by DLTS [22] and L-DLTS [23]. The '*signatures*' of the induced defects (i.e. energy position in band gap relative to the conduction band and the 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 ln (T^2/e) vs. 1000/T, where e is either the hole or electron emission rate, and T is the measurement temperature [24].

3. Results and discussion

3.1. I–V characteristics and germanides formation

The Schottky barrier heights (SBHs) of the contacts were calculated from the I–V characteristics, which were analysed by the thermionic emission (TE) model given by the following equation [25]:

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

where

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

is the saturation current obtained as the intercept from the straight line of ln I vs. V, A^* is the effective Richardson constant, A is the diode area, T the measurement temperature in Kelvin, k is the Boltzmann constant, Φ_B is the zero-bias effective SBH, q is the electronic charge and n is the ideality factor, which can be determined accurately from the slope of the linear part of a ln I vs. V plot. Assuming pure TE, n can be obtained from Eq. (1) as

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

which is equal to unit for an ideal diode but usually has a value greater than unit. The values of zero-bias effective SBH were determined from the intercepts of straight lines of semilog-forward bias I–V characteristics with the help of Eq. (2).

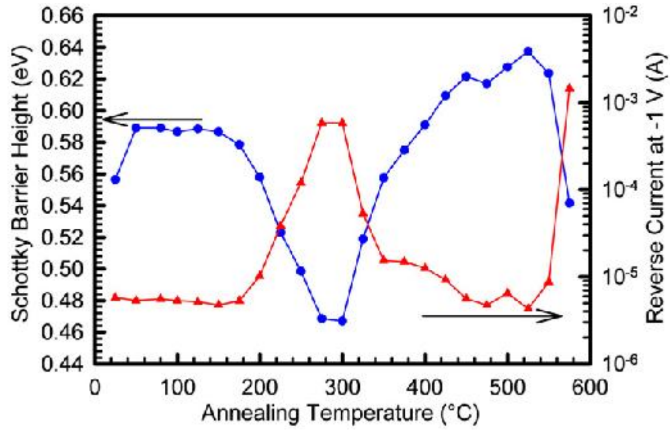

Fig. 1. Plot of the Schottky barrier height and reverse current at −1 V as a function of annealing temperature for Ru Schottky contacts on n-Ge (1 0 0).

Fig. 1 shows the variation of SBH and reverse current at a bias voltage of −1 V with the annealing temperature for Ru Schottky contacts on n-Ge (1 0 0). The values of SBH and reverse current at a bias of −1 V for the as-deposited samples were determined to be (0.557 ± 0.005) eV and (5.79 ± 0.02) μA, respectively. The results (Fig. 1) indicate nearly a constant SBH in the temperature range 50–150 °C. After annealing at temperatures higher than 150 °C the SBH decreases with annealing temperature and a low SBH of (0.467 ± 0.005) eV is achieved after a 275 °C anneal, suggesting a significant reaction between Ru and the Ge substrate forming a germanide. Although Gaudet et al. [7] have reported the first phase Ru germanide, Ru+Ru_2Ge_3, forming at 450 °C after a ramp anneal, we propose that in our case here, after subjecting the Ru Schottky contacts to isochronal annealing, the first phase of Ru germanide is formed in the temperature range 150–275 °C, as SBH decreases significantly above 150 °C annealing. The subsequent increase in SBH after annealing at temperatures higher than 300 °C depicts the formation of the Ru germanide Ru_2Ge_3 [7], in the temperature range 325–525 °C. After a 550 °C anneal the contacts became near-ohmic and further evaluation was impossible.

During the annealing process, Ru may react with Ge. It is well known that the chemical reactions between metals and semiconductors at interfaces can play an important role in the electrical properties of devices. The chemical equilibrium after heat treatment results in interfacial rearrangement, interdiffusion and compound formation, which should have a profound effect on the electronic equilibrium producing the Schottky barrier [26]. Hence, the change in SBH may be due to the combined effects of interfacial reactions and phase transformation. Furthermore, the SBH change in the Schottky contacts can be explained according to the effective work function (EWF) model [27], where the barrier height value is determined by the work function of one or more phases resulting from the MS reactions, which occur during metallisation and annealing, and each phase having its own effective work function [28].

The value of the ideality factor for the as-deposited samples was determined to be 1.08. This ideality factor is almost a constant within the experimental error up to annealing temperature of 175 °C. After annealing at temperatures higher than 175 °C the ideality factor was greater than 1.1. For ideal Schottky contacts the ideality factor is 1.0. The ideality factors for the Schottky contacts found to be greater than 1.1, depicts that the current transport properties are not well modelled by TE alone although these contacts remain rectifying [29]. The deviation from ideality may be attributed mostly to the states associated with defects near the surface of the semiconductor. These interface states, interdiffusion, chemical reaction, compound formation, etc., can all be derived from thermodynamics due to thermal annealing [30,31]. These may lead to recombination centres and SBH inhomogeneities [32], which cause a flow of excess current leading to a deviation from the ideal TE behaviour.

3.2. DLTS analysis of fabrication and annealing process induced defects

3.2.1. Electron traps

DLTS spectra for electron traps induced in Ge after EBD of Ru/ *n*-Ge (1 0 0) Schottky contacts are shown in Fig. 2(**A**). The spectra were recorded for the as-deposited, 100, 150, 175, 200, 225, 250, 300 and 350 °C. After Ru Schottky contacts fabrication, E(0.38) level with a capture cross section of $1.0 \times 10^{-14}\ \mathrm{cm}^{-2}$ is the only detectable electron trap. The defect's electronic properties were extracted from the Arrhenius plot shown in Fig. 3. The electron trap E(0.38) is the well known $(=/-)$ charge state of the E-centre (V–Sb) in the Sb-doped Ge. This E-centre is a very important defect in Ge for its role in dopant deactivation and free carrier removal, as each V–Sb complex formation results in the removal of three free carriers [14]. It is therefore important to establish the annealing mechanism of the E-centre. The defect concentration as a function of depth profile of the E-centre, measured at different isochronal annealing temperatures is shown in Fig. 4. It can be seen that the depth profile for the as-deposited samples shows that the defect concentration decreased from Ge surface, and this proves that the energetic particles emerging from the filament during contact fabrication create vacancies on and beneath the semiconductor [24]. The defect concentration profile (Fig. 4) shows an increase in the defect concentration deeper into the bulk material as the annealing temperature is increased. This is attributed to the diffusion of the E-centre into the semiconductor as it becomes mobile at elevated temperatures. At 175 °C anneal, with prolonged annealing time, results in a broadened profile, which shifted to lower concentration. Therefore, further investigations are needed to be carried out to establish the defect concentration profile model for prolonged time anneal.

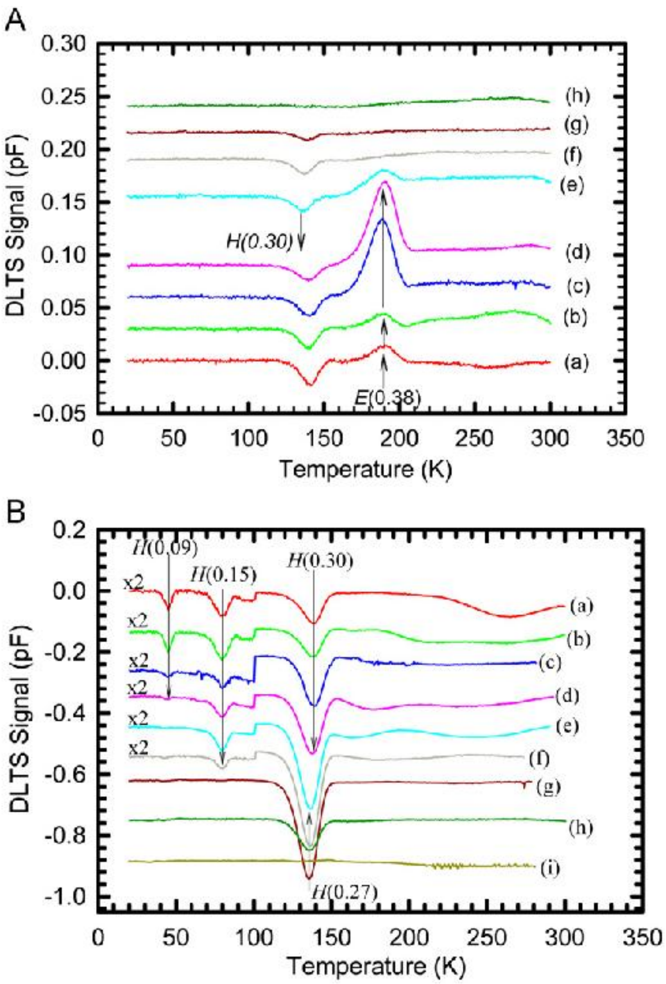

Fig. 2. (**A**) DLTS spectra for electron traps after electron beam deposition of Ru Schottky contacts on *n*-Ge (a) for as-deposited, and after annealing at (b) 100 °C, (c) 150 °C, (d) 175 °C, (e) 200 °C, (f) 225 °C, (g) 250 °C, (h) 300 °C and (i) 350 °C. These spectra were recorded with a quiescent reverse bias of −2 V, at a rate window of $80\ \mathrm{s}^{-1}$, a pulse voltage of −0.15 V and pulse width of 1 ms, **(B)** DLTS spectra for the hole traps induced in *n*-Ge (1 0 0) after electron beam deposition of Ru Schottky contacts. The spectra were recorded with quiescent reverse bias −1 V, at a rate window of $80\ \mathrm{s}^{-1}$, a pulse voltage of 3 V and pulse width of 1 ms.

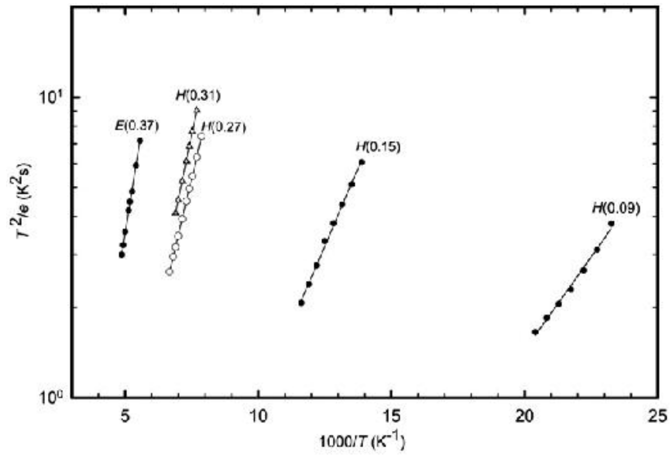

Fig. 3. Arrhenius plot of an electron and hole traps introduced in *n*-Ge (1 0 0) after Ru Schottky contacts fabrication using EBD.

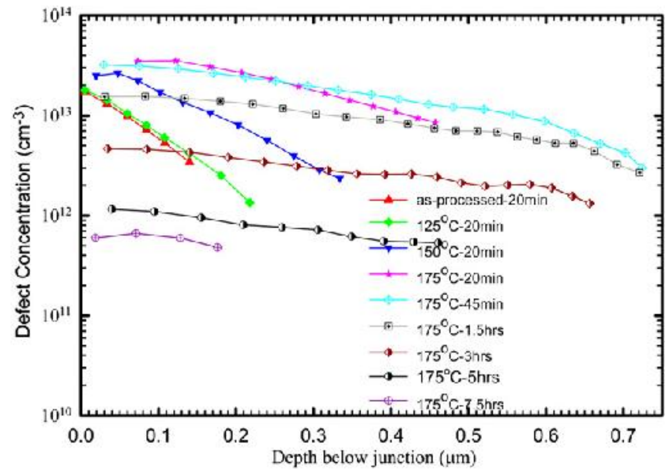

Fig. 4. Depth profile for E(0.38) at different annealing temperatures. The measurements were performed by L-DLTS at fixed temperature of 195 K.

3.2.2. Hole traps

Fig. 2(**B**) shows the DLTS spectra for hole traps introduced in Ge (1 0 0) during Ru Schottky contacts EBD. Hole trap H(0.30) with capture cross section $6.2\times10^{-13}\,cm^{-2}$ is the prominent single acceptor level of the E-centre. The hole traps H(0.09), H(0.15) and H(0.27) with capture cross sections $7.8\times10^{-13}\,cm^{-2}$, $7.1\times10^{-13}\,cm^{-2}$ and $2.4\times10^{-13}\,cm^{-2}$, respectively, were also observed in the as-deposited Ru/*n*-Ge (1 0 0) Schottky contacts. The electronic properties of these defects were obtained from the Arrhenius plots shown in Fig. 3. Auret et al. [10] also reported the trap H(0.09) after metallisation by the EBD process. It has been proposed that this defect is the third charge state of the E-centre (+/0) [33].

Although the hole trap H(0.27) has been reported to be induced after a 200 °C anneal of MeV electron irradiated Ge sample [34], in this study the defect was induced during the Ru Schottky contacts fabrication process. This may be due to the fact that during EBD the substrate temperature is higher than the room temperature and thus thermally inducing the defect H(0.27). The measurement of the hole trap H(0.27) in the presence of H(0.30) was achieved by L-DLTS, which could clearly separate the thermal emission rate signals of these defects, and the peak concentration for H(0.30) trap is higher than that of H(0.27) in the as-deposited samples. The concentration of H(0.27) increased with annealing temperature until it reached a maximum after 225 °C anneal, at which point the E-centre completely vanishes. This confirms what was reported by Coutinho et al. [35] and Markevich et al. [36] that H(0.27) is a product of the annealing of V–Sb to form a new V–Sb_2 complex, which is electrically active [35,36]. After 350 °C annealing temperature all defects had completely annealed out and the annealing was carried out up to 600 °C to determine whether there are any other defect levels that might be reactivated after presumably being transformed into inactive complexes during annealing. There were no other defects observed above 350 °C annealing temperature.

4. Summary

Ru/*n*-Ge (1 0 0) Schottky contacts were fabricated by EBD. The Schottky contacts behaviour was investigated under various annealing conditions. The variation of SBH and ideality factor with annealing temperature may be attributed to interfacial reaction of Ru with Ge and phase transformation of the metal–germanides during annealing. The results show that Ru/*n*-Ge (1 0 0) Schottky contacts are thermally stable over a wide range of temperature. DLTS and L-DLTS revealed that the dominant defect induced by EBD is the V–Sb (E-centre). This depicts that during EBD vacancies are created on and below the semiconductor surface by particles, which are ionised around the filament and then accelerated by electric and magnetic fields towards the substrate. A hole trap H(0.27), induced during EBD of Ru Schottky contacts shows some reverse annealing between room temperature and 350 °C, where it anneals out, reaching a maximum concentration at 225 °C. This trap is reported to be due to V–Sb_2 complex. All defects in Ru Schottky contacts are annealed out after 350 °C.

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