IVC-17/ICSS-13 and ICN+T2007 IOP Publishing
Journal of Physics: Conference Series **100** (2008) 042005 doi:10.1088/1742-6596/100/4/042005

RBS investigation of annealed thin gold layers on crystalline germanium

M. Hayes[1], F. Schrempel[2], S.M.M. Coelho[1], F.D. Auret[1], J.M. Nel[1] and W. Wesch[2].

[1]*Department of Physics, University of Pretoria, Pretoria, South Africa*
[2]*Institut für Festkörperphysik, Friedrich-Schiller-Universität, Jena, Germany*
mhayes@postino.up.ac.za

Abstract. In this work we report firstly on the behaviour of Schottky barrier diodes (SBD's) when subjected to thermal treatment after metallization. To better understand this, a systematic study of the interaction between thin gold films and crystalline germanium substrates was undertaken. Gold metal films having thicknesses of 30 and 100 nm have been prepared by means of thermal evaporation on bulk-grown (111) *n*-type germanium doped with Sb to a level of 2.5×10^{15} cm^{-3}. Before metallization the samples were first degreased and then etched in a mixture of H_2O_2:H_2O (1:5) for one minute. Subsequently the samples have been thermally treated in Ar-atmosphere for 10 minutes and at temperatures ranging from 300 to 600°C. Rutherford backscattering spectrometry (RBS) has been performed to estimate the composition of the as-deposited and thermally treated films. It was found, that the composition of the as-deposited film remains unchanged under thermal treatment up to 340°C. Between 340°C and 360°C a gold-rich layer containing a very small amount of germanium is formed. At 361°C this layer suddenly converts to a germanium-rich layer with a small amount of gold. This transition is accompanied by the formation of agglomerates on the surface of the substrate.

1. Introduction

Germanium has been the preferred host for most of the early studies on defects in semiconductors. The research was driven by the search for sensitive detectors for gamma radiation [1]. Defects and defect formation in Ge, being in the shade over the last two decades, have recently generated new interest because of their potential applications. The low effective mass of holes in Ge has opened up the possibility of using Ge in ultrafast complimentary metal-oxide-semiconductor devices [2]. This, in turn, has sparked renewed interest in the properties of defects in Ge because defects ultimately determine the performance of devices. Germanium-on-insulator (GeOI), which combines high mobility of charge carriers with the advantage of a silicon-on-insulator (SOI) structure, is an attractive integration platform for the future integrated circuit technology. Also, due to its low lattice mismatch with GaAs, III-V compound transistors as well as opto-electronic functions can be integrated on GeOI [3].

To exploit the advantages of germanium an appropriate contact technology will have to be developed. Analogous to the silicon-based technology, where metal silicides are used to obtain low-resistance contacts, contacts made of metal germanides could exhibit low sheet and contact resistance, good stability after heat treatment and could be formed by means of simple technological processes like thermal evaporation at low temperatures. Data concerning the behaviour of metal thin films on germanium upon thermal treatment is relatively scarce. The thin film reactions of 20 transition metals, excluding gold, with germanium substrates have been reported [4]. It was found that among the investigated materials Ni and Pd were the most promising candidates because the formation of NiGe and PdGe at low temperatures lead to contacts with low resistivity, limited film roughness, sufficient thermal stability and limited sensitivity to oxidation. The formation of particularly NiGe contacts has been investigated in some detail [5].

2. Experimental

A bulk-grown (111) 2-inch Ge wafer doped *n*-type with Sb to a level of 2.5×10^{15} cm^{-3} was cut into manageable pieces (3 mm × 5 mm) and degreased in successive trichloroethylene, acetone and methanol ultrasonic baths. After a de-ionized water rinse, the samples are etched in a mixture of H_2O_2 (30%) : H_2O (1:5) for one minute, rinsed again in de-ionized water, and inserted into a vacuum chamber where 100 nm thick AuSb (0.6 % Sb) was resistively deposited on their back surfaces as ohmic contacts. A ten minute anneal at 350 °C in Ar lowers the barrier height and the contact becomes ohmic. Phase two involves the same cleaning and etching procedure as above followed by metal deposition onto the front of the samples. These 0.6 mm diameter Schottky metal contacts are resistively evaporated through a mechanical contact mask to a thickness of 200 nm, thus forming a Schottky barrier diode (SBD). For the topography and RBS measurements, the Ge samples were degreased and etched as described above and 30 nm and 100 nm thick layers were resistively evaporated onto the same side where the Schottky contacts would have been deposited normally. In situ monitoring of the film thickness growth was achieved via an Inficon crystal growth monitor. The first 10 nm of metal was deposited at a rate of 0.1 nm/s to minimise damage to the germanium substrate, with subsequent ramping up to 0.3 nm/s for the remainder of the deposition.

The electrical measurements were performed using a current-voltage (IV) station where measurements are taken under normal atmospheric conditions, at room temperature without the sample being exposed to light. Metal probes are used to make electrical contact with the Schottky diode that is being measured. Composition and structural analyses was performed by utilizing 1.4 MeV He^+ ions from a 2.5 MV Van de Graaff accelerator at room temperature performing Rutherford Backscattering (RBS) in both the random and channeled orientations.

3. Results

Some metallization procedures are known to introduce defects at and close to the metal-semiconductor junction. Defect introduction influences the barrier heights of the contacts and alters device performance [6-9]. These defects are dependant on interacting, energetic species reaching the semiconductor surface and subsequently influencing the device in a positive or negative manner. In order to remove some of these defects, the SBD's were subjected to thermal treatment up to 600 ºC. The quality of the SBD's was tested by measuring the reverse and forward bias I-V characteristics and the results are depicted in figure 1.

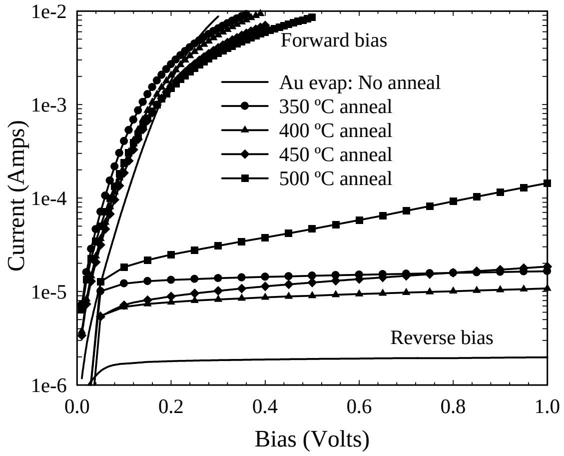

Figure 1. Current-voltage measurements under forward and reverse bias of Au Schottky diodes recorded at 300 K before and after 10 minute annealing in Ar-atmosphere. The Au Schottky contact was 200 nm thick and the AuSb ohmic contact was 100 nm thick.

From this figure we observed only a negligible change in the forward bias characteristics, but an increase in the reverse leakage current with increasing temperature up to 350 ºC. Thereafter, there is a decrease in reverse leakage current up to 400 ºC. After 400 ºC, an increase in the slope of the reverse leakage current is observed up to 450 ºC, where after an increase in both slope of and reverse leakage current is observed.

Along with the change in I-V properties, there was a visible change in the morphology of the contact when viewed at low magnifications under an optical microscope. The cause of this phenomenom was investigated by performing RBS on 100 nm and 30 nm thick Au layers evaporated resistively onto the same side of the Ge as is used for Schottky contact deposition. The RBS spectra 30 nm thick layers are depicted in figure 2.

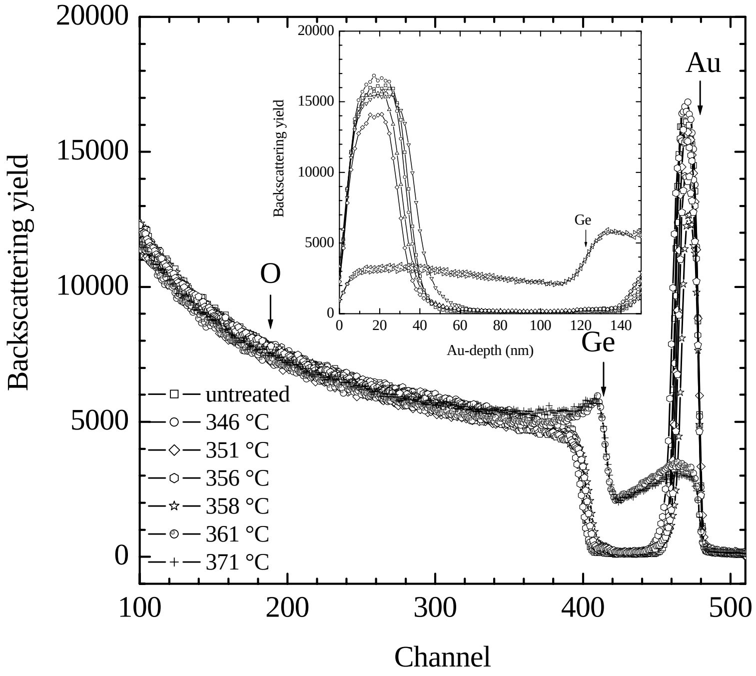

Figure 2. Energy spectra of 1.4 MeV He ions backscattered on 30 nm thick Au-layers deposited on <111>Ge and thermally treated at different temperatures. The inset shows the energy to depth conversion with respect to the Au-surface.

It is clear from figure 2 that between 358°C and 361°C, the distribution of gold on the germanium substrate changes. This is also seen in figure 3, where the atomic percentage of Au and Ge near the surface is plotted as a function of temperature. In this temperature range a eutectic point exists in the Au-Ge system (361 °C and 28 % Ge) [10]. The solid solubility of Ge in Au is 3.1 %, but that of Au in Ge is very low, <10^{-5} % [11]. From figure 3 it can be seen that at temperatures between 350 ºC and 360 ºC, there is an slight increase in the concentration of Ge on the surface, and it is expected that this is due to diffusion of Ge through the gold thin film to the surface, in a similar manner to previously reported polycrystalline thin films of Au and Ge [12, 13]. A sharp increase in Ge content occurs between 360°C and 361°C, which coincides with the eutectic temperature, but the Ge concentration is much higher than expected at the eutectic point. The dramatic change in the distribution of gold and germanium at the eutectic temperature can thus be attributed to the Au-Ge liquid phase which would form at 361°C. From SEM micrographs, not shown here, eutectic Au-Ge island growth is observed with holes around that which lead all that way down to the Ge substrate and the higher than expected Ge signal observed by RBS thus most probably comes from the Ge substrate. However, this still needs to be investigated in more detail. No oxygen content, thus no GeO, was detected using RBS. This is currently being investigated using TOF-SIMS profiles on these films.

Although diffusion is commonly reported for Au/Ge bi-layer systems, where both the Au and Ge layers are polycrystalline, to the authors' knowledge, the diffusion of Ge from the crystalline substrate through the polycrystalline Au layers has not been reported yet. It is also interesting to note that from channeling measurements (not shown here), the polycrystalline Au layers, to a certain extent, align to the crystal structure of the crystalline Ge substrate and it was possible to observe a reduction of more than 30% in the Au peak of the channeled RBS spectra when compared to that in the randomly orientated RBS spectra.

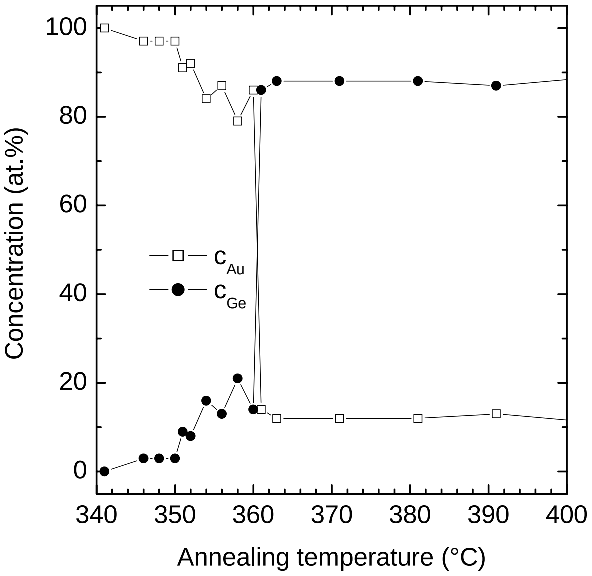

Figure 3. Atomic percentage of Au and Ge near the surface versus annealing temperature for 30 nm thick Au-layers deposited on <111> Ge and thermally treated in a Ar-atmosphere. The concentration was calculated using the WinDF program described in [14].

4. Conclusion

The visible change in the morphology of the Au contacts upon annealing, can be attributed to the segregation of Ge that diffused from the crystalline substrates through the polycrystalline Au layers for temperatures between 350 ºC and 360 ºC. . The dramatic change in the distribution of gold and germanium at the eutectic temperature can be attributed to the Au-Ge liquid phase which would form at 361°C. The higher than expected concentration of Ge might be due to the formation of holes around eutectic Au-Ge islands leading all the way to the Ge substrate.

References

[1] J. Weber, M. Hiller and E.V. Lavrov, Materials Science in Semiconductor Processing **9**, 564 (2006).
[2] *Germanium Silicon: Physics and Materials*, Semiconductors and Semimetals Vol. 56, edited by R. Hull and J. C. Bean, Academic Press, San Diego (1999).
[3] T. Akatsu, C. Deguet, L. Sanchez, F. Allibert, D. Rouchon, T. Signamarcheix, C. Richtarch, A. Boussagol, V. Loup, F. Mazen, J-M. Hartmann, Y. Vampidelli, L. Clavelier, F. Letertre, N. Kernevez and C. Mazure, Materials Science in Semiconductor Processing **9**, 444 (2006).
[4] S. Gaudet, C. Detavernier, A.J. Kellock, P. Desjardins, C. Lavoie, J. Vac. Sci. Technol. **A 24(3)**, 474 (2006).
[5] Q. Zhang, N. Wu, Th. Osipowicz, L.K. Bera, C. Zhu, Jap. J. Appl. Phys. **44** (45), 1389 (2005).
[6] F. D. Auret, O. Paz and N. A. Bojarczuk, J. Appl. Phys. **55** (6), 1581 (1984).
[7] M. Mamor, F. D. Auret, M. Willander, S. A. Goodman, G. Myburg, and F. Meyer, Semiconductor Science and technology **14**, 611 - 614 (1999).
[8] F. D. Auret, S. A. Goodman, F. K. Koschnik, J.-M. Spaeth, B. Beaumont and P. Gibart, Appl. Phys. Lett. **74** (15), 2173-2175 (1999).
[9] G. Myburg and F. D. Auret, J. Appl. Phys. **71**, 6172 (1992).
[10] P-Y Chevalier, Thermochimica Acta **141,** 217 (1989).
[11] G. V. Samsonov and V. N. Bondarev, *Germanides*, Published by consultants Bureau, New York, 52 (1969).
[12] S. Zhang, St. J. Dixon-Warren, S. R. Das, J. Appl. Phys. **95,** 3521 (2004).
[13] S. Ingrey and B. MacLaurin, J. Vac. Sci. Technol. **A 2**, 358 (1984).
[14] N.P. Barradas, C. Jeynes, R.P. Webb, Appl. Phys. Lett. **71,** 291(1997).