Characterisation of Nickel Germanide Formed on Amorphous and Crystalline Germanium

A thesis submitted in fulfilment of the requirements for the degree of
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Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis/project is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

Fahid Alhumaidi Algahtani

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Abstract

Germanium offers unique properties as a semiconductor materials for complementary metal–oxide–semiconductor (CMOS) devices with nearly four times the hole mobility and two times the electron mobility of silicon resulting in higher currents. However, two essential requirements in the application of Ge for CMOS technology are the formation of shallow junctions and the formation of ohmic metal contacts with low resistance.

High diffusivity of dopants in crystalline germanium is a problem when forming shallow junctions. However, amorphisation of crystalline germanium where dopant implants are to occur leads to shallow junctions. In this work both amorphous and crystalline germanium (a-Ge and c-Ge) are investigated. Nickel germanide (NiGe) formed on a-Ge and c-Ge is investigated for material and electrical properties. NiGe has been reported as a suitable germanide for low resistance ohmic contacts on c-Ge. The crystal quality of films formed is poorer for the germanides formed on a-Ge but there is only a slight increase in sheet resistance. The grains of NiGe formed on a-Ge show a growth that is hexagonal like, extending into the substrate further than germanides grains formed on crystalline germanium. The NiGe formed on c-Ge has a much more uniform thickness and uniform grain size and shape.

Thin films of nickel germanide conveniently form at the relatively low temperature of 300C in a matter of minutes and at even lower temperatures over a longer time. This thesis reports on the formation of NiGe on c-Ge substrates at low temperatures (less than 300°C). Ni films deposited on Ge substrates formed NiGe by heating the samples in an atmosphere

nearly void of oxygen. Ni films of thickness 50 to 400 nm were deposited on c-Ge and heat treatments undertaken on samples for time durations of 5 minutes to 12 hours at different temperatures. It was found that thickness of 25nm to 100 nm was not a significant factor and that NiGe formed in a few minutes on c-Ge for this thickness of Ni heated at 300°C. The temperature of formation for 400 nm reacting with germanium was longer. For all thickness of Ni, long durations were required for the lowest temperature of formation which were between 225°C and less than 300°C.

The sheet resistances of NiGe on a-Ge and c-Ge are suitably low for use in CMOS technology. Metal contacts to NiGe were investigated and low resistance contactst were obtained. The contacts to c-Ge were significantly better. Improvements in processing is required for suitably low resistance contacts to be obtained for metal to NiGe formed on a-Ge, but results obtained here are promising and further investigation is warranted. NiGe on a-Ge shows poorer grain crystal quality and improvements in this are likely to lead to contacts with lower specific contact resistivity.

List of Figures

Figure 1.1 NiGe sheet resistance compared with the ITRS target of Source/Drain extension sheet resistance [54].	7
Figure 1.2 Schematic showing the use of a-Ge for a Ge MOSFET, (a) structure for a-Ge, (b) example of boron doped region minimizing the distance that carriers have to travel through a-Ge before travelling through a c-Ge channel under the gate oxide (c) the germanide contact region.	8
Figure 1.3 Phase sequence of the reaction of 30-nm-thick transition metal films capped with a 5-nm-thick a-Ge overlayer deposited on (a) G(001) and (b) a-Ge during a 3 °C s ⁻¹ ramp anneal in purified He. Metal to germanium ratios in each germanide phase are indicated in the color-coded legend [77].	11
Figure 2.1 Schematic of an ion implanter (modified figure from [19])	32
Figure 2.2 Simulation of lateral distribution of germanium ions (9999) into crystalline germanium at energies of 550 keV, 1 MeV and 2 MeV and each for a dose of 1x 10 ¹⁵ cm ⁻² .	34
Figure 2.3 Profile of TRIM Ion range for Ge ions in c-Ge for implantation at 550 keV. The parameters (i) ion range, (ii) straggle, (iii) skewness, and (iv) kurtosis – these are characteristics of the plot.	36
Figure 2.4 Profile of TRIM Ion range for Ge ions in c-Ge for implantation at 1 MeV.	37
Figure 2.5 Profile of TRIM Ion range for Ge ions in c-Ge for implantation at 2 MeV	38
Figure 2.6 Combined profiles of TRIM Ion ranges for Ge ions in c-Ge for implantation at the three energies of 550 keV, 1 MeV and 2 MeV. (The same number of ions was used in each of the three simulations).	38
Figure 2.7 profiles for germanium ions implanted into a germanium substrates at different energies: 550 keV, 1 MeV and 2 MeV (TCAD simulation using analytical model)	40
Figure 2.8 Combined profile for germanium ions implanted into a germanium substrate at different energies: 550 keV, 1 MeV and 2 MeV (TCAD simulation using analytical model)	41
Figure 2.9 HRTEM cross-section image showing the amorphous Ge layer (white arrows), approximately 1.3µm, resulting from ion implantation of Ge with three successive doses of Ge ions of 1x10 ¹⁵ cm ² at 550 keV, 1 MeV and 2 MeV. Also shown is the region where NiGe was formed at the surface.	44

Figure 2.10 HRTEM cross-section image showing the amorphous Ge layer at lower magnification.	45
Figure 2.11 HRTEM cross-section image showing the amorphous Ge layer at higher magnification. The NiGe region at the top is also much more apparent.....	46
Figure 2.12 HRTEM image at high magnification showing the Nickel germanide grains formed in the amorphous germanium	47
Figure 2.13 Electron diffraction pattern of amorphous germanium	48
Figure 2.14 Electron diffraction pattern of crystalline germanium.	49
Figure 3.1 Schematic showing the formation of NiGe on a crystalline germanium substrate. The figure shows that the NiGe formation occurs at the Ni and NiGe interface (initially the Ni and Ge interface). The reaction is complete when all the Ni has reacted. Ge and Ni atoms must diffuse to the reaction site for the reaction to take place.	60
Figure 3.2 Schematic showing the formation of polycrystalline NiGe on a CRYSTALLINE germanium substrate. Note that the resulting NiGe is polycrystalline with a relatively smooth surface and varying depth of grains. The example shown above is for a 100 nm Ni film. The ratio of thickness NiGe to the initial Ni thickness is approximately 2.2	61
Figure 3.3 100 nm Ni on c-Ge and no heat treatment. The Ni was deposited by electron beam evaporation. (Note, the initial surface of the Ge wafers had the same topography as the Ni coated Ge wafers)	62
Figure 3.4 100 nm Ni on c-Ge, 350 °C and 30 minutes heating. Samples were heat treated in a furnace with nitrogen flow and Ti coated polished silicon wafers were also included to getter oxygen.	63
Figure 3.5 100 nm Ni on c-Ge, 350 °C and 90 minutes heating.	63
Figure 3.6 100 nm Ni on c-Ge, 400 °C and 30minutes heating	64
Figure 3.7 100 nm Ni on a-Ge , 350 °C and 30minutes heating	64
Figure 3.8 Combined qualitative and quantitative analysis for 100 nm Ni on a p-type crystalline-Ge 400 C ⁰ for 30 min) sample using: (a) 5 keV, (b) 10 keV, (c) 15 keV, (d) 20 keV.	69
Figure 3.9 Combined qualitative and quantitative analysis for 100 nm Ni on a p-type amorphous-Ge (400 °C for 30 min) sample using: (a) 5 keV, (b) 10 keV, (c) 15 keV, (d) 20 keV.....	72
Figure 3.10 XRD diffractograms of nickel germanides formed at various annealing temperatures. Corresponding phases and their crystallographic orientations are labelled [3].....	73

Figure 3.11 XRD diffractograms at temperatures in the range 200-400 °C for heat treatments on samples with 50 nm Ni deposited in c-Ge. Each successive temperature was held for 5 minutes..	75
Figure 3.12 XRD diffractograms of nickel germanide formed from 50 nm Ni on crystalline and on amorphous germanium, heated for 30 minutes at 300 C	77
Figure 4.1 HR-TEM micrograph for fully reacted 50 nm Ni on c-Ge. The uniformity of the layer can be seen in this figure, as it shows many grains.....	86
Figure 4.2 HR-TEM micrograph for fully reacted 50 nm Ni on c-Ge. The relative smoothness of the surface and the sharp interface between the NiGe grains and the Ge substrate can be seen here. The bottom of the grains is somewhat rounded (compared to the top)	87
Figure 4.4 HR-TEM cross-section micrograph for fully reacted 50 nm Ni on a-Ge. The grain boundaries have been highlighted.	89
Figure 4.5 HR-TEM cross-section micrographs showing increasing magnification images of the NiGe grains formed for fully reacted 50 nm Ni on c-Ge	90
Figure 4.6 HR-TEM cross-section micrographs showing increasing magnification images of the NiGe grains formed for fully reacted 50 nm Ni on a-Ge	91
Figure 4.7 HRTEM cross-section image obtained using hollow cone illumination. There is evidence of recrystallisation in the implanted Ge region below the NiGe grains.....	93
Figure 4.8 HCl cross-section HRTEM image more clearly shows the geometry of the NiGe grains formed.....	95
Figure 4.9 Section of a growing single crystal on an amorphous substrate showing the different growth rates of different faces for a film grown by deposition (modified from ref [13].	95
Figure 4.10 Sequence of the nucleation and texture formation in a polycrystalline film grown by deposition onto an amorphous substrate (modified from ref [13]). t ₁ , t ₂ , t ₃ are growth duration and t ₁ < t ₂ < t ₃ . The web type lines in the top figures indicate the boundary of the growth of crystal layers in particular directions as demonstrated in ref [13] for the model developed.....	96
Figure 4.11 NiGe from Ni on a-Ge growth model developed here, from ref [13]. This model is appropriate for polycrystalline films formed by heat treatment of an already deposited layer (e.g. Ni) on an amorphous substrate (e.g. a-Ge).....	97
Figure 4.12 HRTEM cross section images adapted from Fig 4.6. The suggested growth directions are indicated with the 'web' lines indicating successive stages of growth.	98
Figure 4.13. Three images of electron diffraction patterns of regions in a NiGe on c-Ge sample. On the top left hand side is the image from the Ge substrate (region 10110960). The other diffraction patterns are of different NiGe grains (10110961 and 10110962).	102

Figure 4.14 Electron diffraction patterns of regions in a NiGe on a-Ge sample. The a-Ge image (labelled '10110834') shows that this region is polycrystalline (rings are evident)	103
Figure 4.15 (a) HRTEM cross-sectional image of NiGe formed on c-Ge at 400 °C for 10 minutes. (b) Ni map showing the distinct distribution of Ni following the geometry of the NiGe grain given in the rectangular region outlined in (a).....	104
Figure 4.16 Ni, Ge and O elemental mapping using a HRTEM NiGe-c-Ge sample at different magnification (a) Ni, (b) Ge, (c) O, (d) O, (e) Ni, (f) Ge.	106
Figure 4.17 Ni, Ge and O elemental mapping using a HRTEM NiGe-a-Ge sample at different magnification (a) Ni, (b) Ge, (c) Ni remapped, (d) O, (e) O at higher magnification image.	107
Figure 4.18 HRTEM cross-section image of region of NiGe/a-Ge and two corresponding Ni maps of the same region. The images indicate that there is no obvious connection between features in the region of the a-Ge and the clusters observed in the Ni maps.	109
Figure 4.19 EDS qualitative results for fully reacted 50 nm Ni/c-Ge. The results are for areas sp1, sp2, sp3, sp4, and sp5.	111
Figure 4.20 EDS qualitative results for fully reacted 50 nm Ni/a-Ge. The results are for areas sp1, sp2, sp3 and sp4.....	115
Figure 4.21 EDS qualitative results for fully reacted 50 nm Ni/a-Ge. The results are for areas sp5, sp6, sp7 and sp8.....	116
Figure 4.22 EDS qualitative results for fully reacted 50 nm Ni/a-Ge. The results are for areas sp9, sp10 and sp11.	117
Figure 5.1 Four point probe arrangements and equation for different probe spacing compared to sample size.	127
Figure 5.2 Sheet Resistance versus temperature for different thicknesses of Ni on crystalline Ge (c-Ge) for heat treatments of 5 minutes.....	130
Figure 5.3 NiGe Resistivity versus initial Ni thickness on c-Ge for heat treatments of 5 minutes at 400 °C. Note, at 400 °C the different thicknesses of Ni were fully reacted or almost fully reacted to form NiGe and hence the resistivity values are only effective values for the thicker Ni.....	131
Figure 5.4 NiGe Resistivity versus duration of heat treatment for several heat treatments of initial Ni thickness of 400 nm on c-Ge. The values at lower duration times are really effective resistivity values and above 30 minutes the reaction is clearly complete and the true values of resistivity are determined.....	132
Figure 5.5 Sheet resistance versus temperature for different initial thicknesses of Ni on crystalline Ge (c-Ge) and amorphous Ge (a-Ge) for heat treatments of 5 minutes duration.....	133

Figure 5.6 NiGe Resistivity versus initial Ni thickness on c-Ge for heat treatments of 5 minutes at 400 °C. Note, at 400 °C the different thicknesses of Ni were fully reacted or almost fully reacted to form NiGe and hence the resistivity values are only effective values for the thicker NiGe layers investigated.....	134
Figure 5.7 NiGe Resistivity versus duration of heat treatment for several heat treatments of initial Ni thickness of 400 nm on c-Ge and a-Ge. The values at lower duration times are really effective resistivity values and above 30 minutes the reaction is clearly complete and the true values of resistivity is determined.....	135
Figure 5.8 NiGe sheet resistance versus duration of heat treatment for several heat treatments of initial Ni thickness of 400 nm on c-Ge. This figure uses actual sheet resistance measurements used in Figure 5.7 but without converting the data into resistivity or effective resistivity.	136
Figure 5.9 NiGe sheet resistance versus temperature for 5 minutes duration of heat treatment for 50 nm of initial Ni thickness on a-Ge and c-Ge	137

List of Tables

Table 1.1 Materials Characteristics of alternative channel materials for CMOS devices [65]	5
Table 5.1 Specific Contact Resistivity of Al to NiGe formed on c-Ge and a-Ge	140

Table of Contents

CHAPTER 1.....	1
1.1 MOTIVATION	1
1.2 BACKGROUND.....	2
1.3 GERMANIDE TECHNOLOGY	10
1.4 MAJOR WORKS REPORTED.....	14
1.5 PUBLICATIONS	16
1.6 THESIS OUTLINE	17
1.7 REFERENCES	19
CHAPTER 2.....	31
2.1 MODELLING ION IMPLANTATION OF GE IONS INTO C- GE	33
2.2 EXPERIMENTAL - ION IMPLANTATION OF GE IONS INTO C-Ge	43
2.3 CONCLUSION	50
2.4 REFERENCES	51
CHAPTER 3.....	57
3.1 SAMPLE PREPARATION	58
3.2 ATOMIC FORCE MICROSCOPY (AFM).....	62
3.3 ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS)	66
3.4 X-RAY DIFFRACTION (XRD).....	73
3.5 CONCLUSIONS.....	79
3.6 REFERENCES	80
CHAPTER 4.....	85
4.1 ELECTRON DIFFRACTION	101
4.2 ELEMANTAL MAPPING	104
4.3 ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS)	110
4.4 DISCUSSION	118

4.5 CONCLUSION	120
4.6 REFERENCES	122
CHAPTER 5.....	125
5.1 INTRODUCTION	125
5.2 MATERIALS AND METHOD	126
5.3 RESULTS	129
5.4 SPECIFIC CONTACT RESISTIVITY	138
5.5 CONCLUSION	141
5.6 REFERENCES	143
CHAPTER 6.....	148
6.1 FUTURE WORK	151
6.2 REFERENCE	152
APPENDIX-A.....	153
APPENDIX-B.....	158

Chapter 1

Introduction

1.1 Motivation

As scaling of classical complementary metal-oxide semiconductor (CMOS) devices approaches its fundamental limits, alternative materials and structures must be developed in order to maintain the continuous improvement in device performance. In particular, alternative semiconductor materials with high carrier mobility must be studied to enhance device performance. (Alternative materials and structures for other significant issues that are of need to be addressed include low electrical contact resistance, enhanced thermal conductivity, low and high dielectric constant insulators and diffusion barriers). This thesis is a report on research on low electrical contact resistance technology for germanium

devices. Germanium is back after a 40 year absence as a potential material for current and future CMOS devices. The first semiconductor devices were made from germanium (1950's) but soon silicon took over. The Regency TR-1 was the first commercially manufactured transistor radio, first sold in 1954 [<http://www.regencytr1.com>]. It was made using germanium.

1.2 Background

Recently there has been a resurgence of interest in germanium for semiconductor devices due to the very high electron and hole mobilities that are possible in germanium compared to silicon [1-18]. Incorporation of germanium into CMOS technology is being actively pursued for current and future device nodes [1, 7]. This has partly occurred through the introduction of high permittivity (high- κ) materials for the gate dielectric in standard CMOS processing and a shift away from a reliance on silicon/silicon dioxide structures. The development of new gate-stack materials has opened the way for new materials to be considered for the device channel and germanium is attractive because it offers the possibility of considerably higher mobilities, is viewed as being relatively compatible with current CMOS technology and has the potential to enable performance scaling of CMOS to the end of the current Roadmap [3, 4]. Promising results have been achieved by a number of groups that have fabricated germanium metal oxide semiconductor field effect transistors (MOSFETs) using a variety of gate dielectric materials including GeO_2 , SiO_2 , HfO_2 , ZrO_2 , Al_2O_3 and germanium oxynitride [9-14, 19-34]. However, there are still key challenges to be overcome before the full potential of

germanium MOS devices can be realised. There are a number of fundamental materials and processing issues that need to be solved in order to fully develop Ge CMOS technology.

Key areas that need to be addressed are:

- (i) the need for improved knowledge of appropriate dielectric materials and processes for the gate stack to achieve optimal channel performance,
- (ii) the need to develop and refine suitable metal-germanide contact,
- (iii) the need for suitable dopant activation processes for the source-drain regions of the devices, and
- (iv) The need for process compatibility with the ultrathin Ge layers that are projected to be required for GeMOS technology.

In this thesis the focus is on item (ii) but this is closely linked with item (iii). Despite recent advances [35-64], the gate stack materials and processes need to be further developed so that suitably low defect densities are obtained in the dielectric materials and at the interfaces to allow the projected performance gains associated with germanium channels to be achieved [4].

The ITRS report notes that the gate stack is another difficult challenge for Ge MOSFETs. The materials and processes need to produce low defect densities and be stable at the processing temperatures required during other device fabrication steps including source-drain formation and dopant activation. Also, because of the small band gap of

germanium, band to band tunneling leakage current can be large and it is expected that it will be necessary to use ultrathin Ge layers for the device channel in the form of germanium on insulator (GeOI) or SiGe layered structures. There is currently a lack of knowledge at the level of detail required to be able to identify the most appropriate materials and processes for fabrication of devices in ultrathin Ge layers. The Roadmap also points to the need for marked improvement in materials and processes for the source/drain regions of the devices, especially in the case of n-type material.

To fully exploit the superior charge transport properties of germanium, a low-resistance metal-germanide contact technology needs to be fully developed similar to the self-aligned metal silicide technology that is used in current CMOS processing [4, 15]. Data is needed on the optimal materials and processing conditions to achieve high quality, low-resistance metal-germanide contacts. This includes detailed knowledge of the phases formed as a function of processing temperatures, the reaction kinetics, the growth morphology of the germanide and the quality of the germanide/germanium interface and appropriate impurity doping strategies to achieve high levels of electrical activation of dopants in the contact region immediately below the germanide/germanium interface.

Because Ge has a low bandgap and (compared with Si) Ge devices cannot operate at temperatures above 50C which was a disadvantage in car radios for example in the 1950's. Germanium's sensitivity to temperature means it had limitations in its usefulness when there was not adequate cooling of the Ge chips. The main advantage of silicon was

its high quality native oxide and this was used as the Oxide in Metal-Oxide-Semiconductor devices for decades. Materials with high dielectric constants (Hi-K) are required for CMOS devices. HfO_2 and Al_2O_3 are examples of suitable Hi-K gate dielectrics and these can be deposited on either Si or Ge. Germanium offers nearly four times higher hole mobility and two times higher electron mobility than silicon and this gives rise to larger electrical current.

As stated in the 2011 edition of The INTERNATIONAL TECHNOLOGY ROADMAP FOR SEMICONDUCTORS (ITRS):

“Among those emerging materials potential solutions targeted at enhancing channel mobility are strained Si, germanium (relaxed and strained), and carbon nanotubes”.

Also stated in the ITRS section on Front End Processes

“Germanium as a channel replacement material has attracted great attention because of its excellent electron and hole mobilities. In particular, the hole mobility of strained germanium is much better than that of silicon.”

Table 1.1 Materials Characteristics of alternative channel materials for CMOS devices [65]

	Ge	Si	GaAs	InSb	InP
Bandgap, E_g (eV)	0.66	1.12	1.42	0.17	1.35
Electron affinity, χ (eV)	4.05	4.0	4.07	4.59	4.38
Hole mobility, μ_h ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	1900	450	400	1250	150
Electron mobility, μ_e ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	3900	1500	8500	80 000	4600
Effective density of states in valence band, N_v (cm^{-3})	6.0×10^{18}	1.04×10^{19}	7.0×10^{18}	7.3×10^{18}	1.1×10^{19}
Effective density of states in conduction band, N_c (cm^{-3})	1.04×10^{19}	2.8×10^{19}	4.7×10^{17}	4.2×10^{16}	5.7×10^{17}
Lattice constant, a (nm)	0.565	0.543	0.565	0.648	0.587
Dielectric constant, k	16.0	11.9	13.1	17.7	12.4
Melting point, T_m ($^\circ\text{C}$)	937	1412	1240	527	1060
Clarke number (%)	6.5×10^{-4}	25.8	Ga: 1×10^{-3} As: 5×10^{-4}	In: 1×10^{-5} Sb: 5×10^{-5}	In: 1×10^{-4} P: 8×10^{-2}

In CMOS technology Ge is already important for increasing the mobility of carriers in the channel region by using SiGe. Ge is now viewed as being relatively compatible with silicon CMOS technology [4-5]. Table 1 shows the properties of Ge and other semiconductor materials. The main properties to note are the much higher mobility for holes in Ge compared to all other semiconductors and the higher electron mobility compared to Si. More than three times difference in the mobility of holes and electrons in Si causes restraints for integrated circuit design engineers. For Ge the difference is less than two times and both mobilities are much higher than in Si. Other parameters to note are the low bandgap of Ge which causes heat sensitivity. 0.66eV is much less than the 1.12eV of Si and restricts Ge device operation to about 60 or 70° C.

A good rule of thumb is that the maximum operating temperature (K) is about 500 times the bandgap in eV which gives a value of about 60°C for Ge and 290°C for Si, hence leakage current increase with temperature for conventional consumer electronic devices is generally not a problem with Si devices but is for Ge devices. The effective density of states in the conduction and valence bands are lower for Ge compared to Si but this is not a significant factor in realizing Ge devices. Another property that is very significant is the Clarke number. This number compares the relative amounts of elements near the surface of the earth (meaning what can be procured for processing). Si is abundant and hence it is relatively cheap. Ge is not abundant and hence it is expensive and therefore high volume production of Ge devices on Ge wafers is not viable. Hence Ge on insulator substrates are being developed. Ge on sapphire is an example of such a substrate and this has been developed by the Microelectronics group at Queens University Belfast [16].

Figure 1.1 NiGe sheet resistance compared with the ITRS target of Source/Drain extension sheet resistance [54].

The advantages of Ge, in regard to relatively high carrier mobility for both holes and electrons, are offset by disadvantages and some are more difficult to overcome than others. Its cost of wafer production cannot compete with Si but this can be overcome by using it as a deposited epitaxial layer on Si or other substrates or as has been used extensively, as a combined SiGe semiconductor region on Si substrates. Its sensitivity to heat can be countered by heat sinking. Ge has another disadvantage compared to Si. The relatively high diffusivity of dopants (e.g. boron) in crystalline Ge is difficult to control and increases processing complexity.

Figure 1.2 Schematic showing the use of a-Ge for a Ge MOSFET, (a) structure for a-Ge, (b) example of boron doped region minimizing the distance that carries have to travel through a-Ge before travelling through a c-Ge channel under the gate oxide (c) the germanide contact region.

One method to limit the diffusion of boron after ion implantation is pre-amorphization [66-70]. In [66] the implant and anneal condition for boron as a p-type species in germanium is described. The boron is easier to activate when a pre-amorphization with Ge is done before the boron implantation. A complete re-crystallization of the Ge amorphous layer can be obtained at temperatures as low as 400 °C. In this thesis the process of pre-amorphisation is examined and its effect on the formation of low resistance contacts to Ge devices.

Low resistance contacts are ideally formed using a germanides and the most effective germanide reported is nickel germanides with stoichiometry NiGe. Figure 1.1 shows the sheet resistance of NiGe as a layer in Ge CMOS devices. In addition to low sheet resistance, the contact resistance of NiGe to Ge is much lower than for any metal on its own, much like the use of silicides in Si CMOS technology. NiGe helps to minimize contact and series resistance in Ge CMOS devices.

Figure 1.2 shows the use of amorphised Ge and a germanide to form the source and drain regions of a Ge MOSFET. The purpose of a-Ge is to reduce the diffusivity of the boron dopant leading to desired shallow junctions (Diffusivity of dopants is high in c-Ge).

1.3 Germanide technology

Figure 1.3 is from a paper by Gaudet et al [77], and results from a thorough investigation of many germanides. A germanide is a compound formed by reacting a metal with germanium (similar to forming a silicide by reacting a metal with silicon). The results of this work clearly identified NiGe as the germanide of choice for use as a contact layer in Ge CMOS technology because of the low temperature of formation, stability of the NiGe phase over a large temperature range and (not shown in the figure) the low resistivity of NiGe, compared to other germanides.

In this thesis the focus will be on NiGe as a contact layer for crystalline Ge (c-Ge) and amorphous (a-Ge). a-Ge can be subjected to annealing after dopant implantation and Ni deposition to realize dopant activation, recrystallization (solid phase epitaxy) and NiGe formation.

Figure 1.3 Phase sequence of the reaction of 30-nm-thick transition metal films capped with a 5-nm-thick a-Ge overlayer deposited on (a) G(001) and (b) a-Ge during a 3 °C s⁻¹ ramp anneal in purified He. Metal to germanium ratios in each germanide phase are indicated in the color-coded legend [77].

Obtaining good source and drain contacts and a stable gate dielectric (the native Ge oxide is water soluble) are the key issues for Ge CMOS device fabrication. From a processing point of view, the gate stack must maintain its integrity throughout the source/drain (S/D) junction anneal. N-channel Ge MOSFETs pose a particular fabrication challenge: there is a relatively small process window to achieve both a stable gate stack and a well-activated n⁺ S/D because of the low dopant solubility in Ge and fast dopant diffusion during activation [14].

Much research has been reported on high performance pMOSFETS but not for nMOSFETS. Ge pMOSFETS are good candidates for future generation MOSFETS but the performance of n-channel Ge MOSFETs needs substantial improvement [4-5]. However, Schottky Barrier MOSFETS (Schottky barrier source and drain contacts) have been reported as a viable technology. These require germanide formation to give suitably low barrier heights for electrons. Germanides also give low sheet resistance in the contact regions, like silicides do in Si technology.

Forming ohmic contacts to n-type germanium can be addressed through better control of ion implantation. The technique of pre-amorphization implantation (PAI) has been reported with success by Chao et al [58]. This leads to improved activation of n-type dopant leading to ohmic contacts. This technique can also lead to lower Schottky barrier heights for n-type germanium. The study [71] has reported that through the use of PAI, good ohmic contacts can be readily formed on p-type Ge. For n-type Ge, investigation into

minimising dopant diffusion during re-crystallisation and dopant activation heat treatments is required. Dopant segregation is also an issue in conjunction with forming a germanide for ohmic or Schottky contacts. The position of the peak dopant (and carrier concentration) should occur at the germanide-to-Ge interface to get the lowest interfacial resistance (specific contact resistance). This has been investigated (with SIMS) by Mueller et al [72]. The use of pre-amorphization reduces the depth of the peak dopant concentration and hence the junction depth and depth of germanides below the substrate surface.

The switching time of a MOSFET is related to how fast a charge carrier can move and hence current flow is detected sooner, after the gate signal has been applied to the MOSFET. As stated in the ITRS scaling of MOSFETs is likely to require alternate channel materials in order to continue to improve performance and the next materials of choice seems to be III-V materials or/and germanium. However III-V semiconductor materials are more complex to process and germanium is now viewed as being relatively compatible with silicon CMOS technology and more likely to be further developed as part of Si MOSFET technology.

The resistance of ohmic (obeys Ohm's law) contacts can be a significant part of the parasitic resistance of semiconductor devices. It is important to continue researching ohmic contacts and developing them so that their resistance is as low as possible. Contact resistance is a limiting factor in a microelectronic circuit and it can affect the value of voltage levels in logic circuits for example. Current passing through a contact with a

relatively high contact resistance may cause too high a voltage drop across the contact and hence loss of the information that a signal was meant to have. As electric circuits are getting smaller this issue is becoming more important making it imperative to search beyond the self-aligned silicide contacts used in conventional CMOS silicon semiconductor devices. The self-aligned silicide process for making ohmic contacts has been widely used with the Si MOSFETs to improve certain characteristics. Therefore suggesting that self-aligned Germanides for Ge MOSFETs will behave in a similar, if not better way Zhang et al [73].

1.4 Major works reported

In this PhD thesis, the author demonstrates:

- 1) The processes for forming nickel germanide layers of *minimum electrical resistivity and minimal sheet resistance*.
- 2) The formation of NiGe on *crystalline and amorphous* Ge (c-Ge and a-Ge) was investigated and conditions for forming both at minimal processing temperature was investigated and reported.
- 3) The effects of time duration and temperature on the formation process are reported.

4) Additional work included finite element modeling to obtain accurate sheet resistance values from four point probe measurements on small pieces of Ge substrate with NiGe layers formed on top. Investigation of the amorphisation process was done using the software SRIM (Stopping Range of Ions in Matter) and a suite of materials analysis tools were used to undertake analysis of the cross-sections, surfaces and element composition of the NiGe layers investigated.

Characterizing Nickel Germanide (NiGe) for Electrical Contacts to Germanium Semiconductor Devices

Aim: To characterize Nickel Germanide (NiGe) polycrystalline thin film formation by investigating materials and electrical properties.

Outcomes: The findings of this study indicate the optimum conditions of NiGe formation for different initial Ni thicknesses and optimizing the conditions for minimum temperature and time required to form NiGe.

1.5 Publications

List of Publications

1. F. Algahtani, M. Blackford, E. Pirogova, A. S. Holland. **Optimizing the thermal budget for forming nickel germanide on crystalline germanium.** *Proc. of SPIE. Micro/Nano Materials, Devices, and Systems*, edited by James Friend, H. Hoe Tan, Vol. 8923, doi: 10.1117/12.2034001
2. F. Algahtani, K. B Thulasiram, N. F. M. Nasir, A. S. Holland. **Four point probe geometry modified correction factor for determining resistivity.** *Proc. of SPIE. Micro/Nano Materials, Devices, and Systems*, edited by James Friend, H. Hoe Tan, Vol. 8923, doi: 10.1117/12.2034057
3. Y. Pan, A.M. Collins, F. Algahtani, P.W. Leech, G.K. Reeves, P. Tanner, A.S. Holland. **Investigating extremely low resistance ohmic contacts to silicon carbide using a novel test structure.** *Proc. of SPIE. Micro/Nano Materials, Devices, and Systems*, edited by James Friend, H. Hoe Tan, Vol. 8923, doi: 10.1117/12.2033910
4. S. Almalki, F. Algahtania, M. Blackford, M. S. Alnassar, B. C. Johnson, J. C. McCallum, A. S. Holland, **Investigation of amorphisation of germanium using modeling and experimental processes.** *Proc. of SPIE. Micro/Nano Materials, Devices, and Systems*, edited by James Friend, H. Hoe Tan, Vol. 8923, doi: 10.1117/12.2035093
5. F. Algahtani, P.W Leech, G.K Reeves, A.S Holland, M. Blackford, G. Thorogood, J. C McCallum, B. C Johnson. **Low Temperature of formation of Nickel Germanide by reaction of Nickel and Crystalline Germanium.** *Mater. Res. Soc. Symp. Proc. Vol. 1,2014 Materials Research Society DOI: 10.1557/opl.2014.408*
6. F. Algahtani, M. Blackford, M.S.N. Alnassar, G.K. Reeves, P. Leech, E. Pirogova and A.S. Holland. **Low Temperature of Formation of Nickel Germanide on Crystalline Germanium.** *Proc. 29th International Conference on Microelectronics IEEE-MIEL 2014, BELGRADE, SERBIA, 2014*
7. F. Algahtani, E. Pirogova, A. Holland, M. Blackford, J.C McCallum and B. C Johnson. **Characterisation of Nickel Germanide formed on Amorphous and Crystalline Germanium.** *IEEE-ICSE2014 Proc. 2014, Kuala Lumpur, Malaysia*

1.6 Thesis Outline

These are the major chapters listed in this thesis:

Chapter 1 - presents a general introduction describing the overall aim and objectives of this PhD project.

Chapter 2 - Describes amorphization of Ge including ion implantation modeling and also includes the fabrication of NiGe samples for materials and electrical characterization. Different thicknesses (25nm to 100 nm) of Nickel were deposited on to a p or n type Germanium substrate with the crystal orientation of (100). 1cm x 1cm samples (other sizes will also be used, depending on the subsequent characterization tool to be used) in a vacuum oven for the desired time duration and temperature.

Chapter 3 - describes the surface characterization processes, the experimental work done and the results obtained. Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) were used to characterize the germanide surface and Energy Dispersive X-ray Spectroscopy (EDS) and 2- θ X-ray Diffraction (XRD) were used to study the element composition and crystal structure of the germanides formed and the effects of amorphisation on the germanium substrates used before and after heat treatments.

Chapter 4 - discusses the characterization of NiGe and c-Ge and a-Ge using cross-sectional samples prepared for High Resolution Transmission Electron Microscopy (HRTEM) specifically. The TEM analysis was carried out using high-resolution imaging, electron energy loss spectroscopy (EELS) imaging, EDS analysis, and hollow cone illumination

Chapter 5 - presents the electrical characterization of NiGe thin films. This chapter describes the influence of amorphisation and heat treatments on the sheet resistance of the NiGe formed and on metal contacts to NiGe.

Finally, *Chapter 6* comes to the summarization of thesis and suggestions for possible future works.

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Chapter 2

AMORPHISATION OF CRYSTALLINE GERMANIUM

This chapter reports on the amorphisation of the near surface region of crystalline germanium substrates. The motivation behind the amorphisation process, which is done by ion implantation of germanium ions at high dose (above the amorphisation threshold), is that shallow junctions of doped germanium formed by ion implantation of boron or phosphorous for example are difficult to obtain (compared with doping in silicon technology) [1-8]. Pre-amorphisation (before ion implantation with desired dopant, n or p-type) and subsequent annealing is a realistic process for forming shallow junction in germanium [9-18].

In this chapter, the modeling and process parameters determined for forming a suitable amorphous region of germanium are presented. The desired amorphous region is

of the order of one micron in thickness. In this study the formation of nickel germanide contacts is the focus and one micron of amorphous germanium is sufficient for forming nickel germanides layers from 50 nm, 100 nm, 200 nm and 400 nm of nickel as the amount of germanium consumed is about 1.2 times the initial nickel thickness. The resulting surface of the NiGe is approximately the same as the initial Ni surface.

Figure 2.1 Schematic of an ion implanter (modified figure from [19])

A schematic of an ion implanter is shown in Figure 2.1. The first basic element is the ion source. This may be a solid piece of germanium that is ionized and directed towards the acceleration line. The steering is done by an appropriately selected magnetic field to just make germanium singly charged ions enter the acceleration line which can be tuned to give the germanium ions particular energies for implanting into the target. The target in this case is a crystalline germanium substrate. There is a change in direction at the end of the

ion beam acceleration line. This indicates that only germanium ions will be steered towards the target. Any neutralized germanium ‘ions’ will not be steered. This helps to give more accurate dose measurements as only ions are detected (and effectively counted) in the sampling of the beam that is done to determine and control the ion dose that the target gets.

2.1 Modelling ion implantation of Ge ions into C-Ge

It is beneficial to achieve suitably high electrical activation of n-type dopants in the source-drain contacts by using a pre-amorphisation implant step, typically via Ge implantation, prior to dopant incorporation [10-15]. The amorphous layer can be crystallised at relatively low temperatures $\sim 400^{\circ}\text{C}$ via solid-phase epitaxial recrystallization [16-18] whilst achieving considerable improvement in the dopant activation. At present, this approach to dopant activation has not been coupled with germanide formation. Germanide formation on amorphous Ge (a-Ge) has been observed to lower the crystallisation temperature, a process termed metal-induced crystallisation [9, 18]. Previous work on the measurement and modelling of the effects of dopants and hydrogen on solid phase epitaxy in Ge and other similar studies have shown that the presence of dopants also leads to enhancement of the crystallisation rate [20-37].

Thus, a combination of processes needs to be understood in order to develop a complete picture of crystallisation and dopant-activation during germanide formation and

this information is completely lacking at present. Therefore the study of amorphisation of Ge for shallow junction formation is an important area of study.

There were two simulation tools available for this project. These are TRIM and TCAD from Synopsis. Monte Carlo simulation is used in TRIM and TCAD can use both Monte Carlo and analytical solutions to obtain implantation profiles. Of particular interest is the depth of the implant, and where the concentrations are high enough to cause amorphisation. Unfortunately, TCAD cannot do Monte Carlo simulation of Ge into Ge but can for other ions. There are differences in the projected range given by the between the two techniques, but this difference is not significant in this study.

Figure 2.2 Simulation of lateral distribution of germanium ions (9999) into crystalline germanium at energies of 550 keV, 1 MeV and 2 MeV and each for a dose of $1 \times 10^{15} \text{ cm}^{-2}$.

This section reports on the investigation of the amorphisation of c-Ge using TRIM for ion implantation modelling [38-40]. TRIM stands for Transport of Ions in Matter and is

a software program within an ion implantation program package called SRIM, Stopping and Range of Ions in Matter. TRIM is used universally to determine ion range profiles based on input parameters of ion type and energy and the material of the target layer. Figure 2.2 shows the profile of Ge ion distribution in a Ge substrate for ions implanted at a point with three different energies. The plane of the substrate surface is the x-y plane and the x and y profile for ion depth will be the same. (The z direction is usually regarded as depth into the substrate.). Ion implantation is done over an area in this study that allows for a uniform dose per cm^2 . Hence the information in Figure 2.3 to 2.6 is more useful and the distribution across the doped layer can be considered uniform. Figure 2.4 shows the profile at any region (away from the edges) of the doped layer. The projected range (where the concentration is highest) is an important parameter as well as the distribution itself. Figure 2.5 and 2.6 clearly show the project ranges and profiles at higher energies. In Figure 2.3 there are several parameters given but and ion range is the parameter of most interest. Straggle is the same as standard deviation in a Gaussian plot, skewness indicates which way (towards the surface or into the substrate) the profile deviates from a perfect Gaussian and kurtosis is a measure of the flatness of the plot (again deviating from a perfect Gaussian).

Figure 2.3 Profile of TRIM Ion range for Ge ions in c-Ge for implantation at 550 keV. The parameters (i) ion range, (ii) straggle, (iii) skewness, and (iv) kurtosis – these are characteristics of the plot.

These figures show the profiles at any region (away from the edges) of the doped layer. The projected range (where the concentration is highest) is an important parameter as well as the distribution itself. Figures 2.5 and 2.6 clearly show the project ranges and profiles at the higher energies.

Figure 2.4 Profile of TRIM Ion range for Ge ions in c-Ge for implantation at 1 MeV.

The combination of subsequent Ge ion implantations is shown in Figure 2.6 and this represents what was done in reality. The 550 keV energy dose was done first, then 1 MeV and then the 2 MeV. TRIM does not allow for modifying the germanium properties when successive implants may effectively be interacting with modified germanium (sub amorphous or amorphous), damaged material, likely giving different stopping parameters to for the implanted ions. However, the cross-section high resolution transmission electron microscope images show agreement with the simulations.

Figure 2.5 Profile of TRIM Ion range for Ge ions in c-Ge for implantation at 2 MeV

Figure 2.6 Combined profiles of TRIM Ion ranges for Ge ions in c-Ge for implantation at the three energies of 550 keV, 1 MeV and 2 MeV. (The same number of ions was used in each of the three simulations).

Simulations using TCAD were also undertaken. TCAD can do analytical and Monte Carlo solutions for germanium into germanium but TRIM can only do Monte Carlo. The following figures show different profiles for the implanted germanium ions. The ion range (also called the projected range) is shown as being shallower when determined using the analytical modeling solution. What is most significant is the concentrations which are just above or just below the amorphisation threshold for germanium. The range given by TRIM for Ge implanted at 2 MeV is 1.01 μm whereas the TCAD analytical simulation gives approximately 0.83 μm (Figure 2.7).

However, overall the germanium ions are shown to implant much deeper into the substrate and the concentrations given in the TCAD simulations are of an order to cause amorphisation to a depth below 1 μm . In the following section an experimental study is presented and the amorphisation region is indicated in High Resolution Transmission Electron Microscopy cross-section images.

Figure 2.7 profiles for germanium ions implanted into a germanium substrates at different energies: 550 keV, 1 MeV and 2 MeV (TCAD simulation using analytical model)

Figure 2.8 Combined profile for germanium ions implanted into a germanium substrate at different energies: 550 keV, 1 MeV and 2 MeV (TCAD simulation using analytical model)

The combined effect of the three implantations into germanium is shown in Figure 2.8 for the TCAD simulation. This simulation suggests a sharp drop in implanted germanium ion concentration between 1 μm and 1.2 μm with the concentration going from approximately $1 \times 10^{17} \text{ cm}^{-3}$ to about $2 \times 10^{14} \text{ cm}^{-3}$. This would suggest that there would be a

change in crystal structure near to this thickness. In the TCAD Sentaurus Process, either analytic functions or the Monte Carlo (MC) method can be used to compute the distribution of implanted ions and the implantation damage. However the MC method is not available for germanium ions into germanium. In the Appendix to this chapter, an example is given to show the discrepancy between the simulation methods.

In the TCAD modeling used, analytic implantation models use the simple Gaussian and Pearson functions as well as the advanced dual-Pearson functions. The algorithms for analytic implantation are integrated in Sentaurus Process. The implantation damage with analytic models is calculated according to the Hobler model [41]. The Monte Carlo method uses a statistical approach to calculate the penetration of implanted ions into the target and the accumulation of crystal damage based on the binary collision approximation [42]. The engine for MC implantation is Sentaurus MC [43].

2.2 Experimental - ion implantation of Ge ions into C-Ge

Figure 2.9 shows a high resolution transmission electron microscope (HRTEM) image of a cross-section of a germanium substrate that was ion implanted with Ge ions at equal doses and at the energies used in the simulations. There is a distinct shading change (suggesting the amorphous region changing to the sub-amorphous region) at approximately 1.3 μm thick. This is of the correct order of thickness as expected from ion implantation modeling of the combined effect of the three energies used (550 keV, 1 MeV and 2 MeV). The actual ion implantation dose was $1 \times 10^{15} \text{ cm}^{-2}$ at each energy value. The NiGe layer formed from 50 nm of Ni is also shown in Figure 2.7 and adds to the thickness approximately 5% of what is shown (i.e. the actual amorphous region immediately after ion implantation was approximately 5% less than that shown).

Figure 2.9 HRTEM cross-section image showing the amorphous Ge layer (white arrows), approximately 1.3 μm, resulting from ion implantation of Ge with three successive doses of Ge ions of $1 \times 10^{15} \text{ cm}^{-2}$ at 550 keV, 1 MeV and 2 MeV. Also shown is the region where NiGe was formed at the surface.

It is remarkable that there is a distinct and sharp change of shading (and reasonably close to what the TRIM and TCAD modeling indicates gives for the approximate ion implant thickness). It is assumed that the undamaged crystalline germanium region and the amorphous region will give different effects with regard to electrons transmitting through the material, indicating that the shading interface shown corresponds to the regions above and below the amorphisation concentration threshold.

There are no published results for what the amorphisation concentration threshold is. Amorphisation threshold is usually given as a particular dose, above which amorphisation of a particular substrate by a particular ion occurs. What the actual shading regions corresponds to exactly have not been determined, but considering it is obtained from transmitting electrons through a thin sample (approximately 20 nm), then the shading change is likely indicative of the amorphous germanium region.

Figure 2.10 HRTEM cross-section image showing the amorphous Ge layer at lower magnification.

Figure 2.11 HRTEM cross-section image showing the amorphous Ge layer at higher magnification. The NiGe region at the top is also much more apparent.

Figures 2.10, 2.11 and 2.12 are lower and higher magnification images of the HRTEM image in Figure 2.9. Figure 2.10 shows further that the crystalline (and sub-amorphous region) gives a uniform shading, further confirming that there are two distinct regions for the electrons to transmit through. Figures 2.11 and 2.12 are higher magnification images and show that the shading is not uniform in the amorphised region (unlike the crystalline region). The sample has been heated to 400 °C to form the NiGe and the grains of this layer are apparent.

The variation in shading in the amorphous region indicates that there are clusters where either similar damage has occurred and extends over many atomic lengths, many

atomic layers. The germanide formation may also have an influence on this, but the 'damage clusters' shown as dark spots, occurs relatively far from the NiGe layer.

Figure 2.12 HRTEM image at high magnification showing the Nickel germanide grains formed in the amorphous germanium

Figures 2.13 and 2.14 are electron diffraction images taken in the amorphous region and in the undamaged crystalline germanium. The pattern for crystalline germanium is as expected and near perfect. The pattern for ion implantation damaged 'amorphous' germanium shows that there is some polycrystalline effects. The appearance of rings indicates this. If there were no rings, this would indicate no order at all, i.e. no conglomeration of 'tiny' single crystals (polycrystals). It is understood that the term amorphous is not strictly applied much like the word vacuum which means the complete

absence of anything, yet scientists often refer to degrees of vacuum (e.g. ultra high, high and low vacuum) and similarly with amorphisation.

Figure 2.13 Electron diffraction pattern of amorphous germanium

Figure 2.14 Electron diffraction pattern of crystalline germanium.

2.3 Conclusion

The TRIM simulation of the three successive Ge ion implantations clearly represents the actual ion implantation. What is not clear from the HRTEM cross-sectional image is the variety of damage done to the c-Ge substrate. This could be shown by taking electron diffraction images at different depths to show if the damage corresponds with the different concentrations in the combined profile.

What is of particular note is the sharp interface between amorphous (damaged) and sub-amorphous (much less damaged or undamaged) germanium crystal. The HRTEM images clearly show a uniform depth for the amorphous layer and no randomness is suggested which is what is expected for uniform dose. The simulation profile for the 2 MeV implant shows that there is a significant amount of Ge ions that extend beyond 1.3 microns but the HRTEM images suggest that these are not at a concentration to cause amorphisation of the c-Ge. (The region immediately below the interface is sub-amorphous and gradually with depth becomes the original unaffected by implantation germanium crystal).

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Chapter 3

MATERIAL CHARACTERIZATION 1 – TECHNIQUES REQUIRING SURFACE PREPARATION ONLY:

Atomic Force Microscopy, Energy Dispersive X-Ray Spectroscopy and X-ray Diffraction

Materials characterisation of the surface of the nickel germanide formed was undertaken to study the suitability of nickel germanide as an ohmic contact material. It is important that the surface texture be appropriate for integrating this material in process steps for germanium MOS devices for example. Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) were used to characterise the germanide surface and

Energy Dispersive X-ray Spectroscopy (EDS) and 2- θ X-ray Diffraction (XRD) were used to study the element composition and crystal structure of the germanides formed and the effects of amorphisation on the germanium substrates used before and after heat treatments. Surface characterisation of NiGe on c-Ge has previously been reported [1-11]. This chapter reports on surface characterisation of NiGe using both c-Ge and a-Ge.

The c-Ge material could easily be probed electrically but good ohmic contacts using NiGe had to be made to the a-Ge layer of implanted samples in order to undertake electrical measurements on it, to consider its effect on NiGe sheet resistance.

3.1 Sample Preparation

Samples for investigating NiGe formation were prepared from n and p-type crystalline germanium (c-Ge) wafers with resistivity 0.05 and 30 Ω .cm respectively. The wafers were diced into suitable sizes (typically 1cm x 1cm and 1.5 x 1.5 cm) and the polished surfaces of the germanium samples were cleaned in AZ 100 solvent at 80 °C for 15 minutes followed by acetone, isopropyl alcohol and deionized water and dried by pressurized nitrogen gas and followed by soaking in a 10% HF solution and further drying by pressurized nitrogen gas. Ni thicknesses of 50 nm, 100 nm, 200 nm and 400 nm were deposited by electron-beam evaporation on crystalline germanium and heat treatments undertaken on several samples of each thickness for different temperatures with time durations of 1 minute to 20 hours. After annealing, the samples were characterized by

different materials surface analysis techniques: Energy Dispersive X-Ray spectroscopy (EDS) in a Scanning Electron Microscopy (SEM) system, Atomic Force Microscopy (AFM) and X-ray Diffraction (XRD). The results obtained by TEM analysis have included high resolution cross-sectional images. The fabrication required for the above processes and for sheet resistance of the NiGe layers, was dicing, cleaning, metal deposition and heat treatments. The sheet resistance of the germanides was measured by the four point probe and the Van der Pauw techniques. Using the Van der Pauw technique, the amorphous Ge layer's electrical properties were also investigated. Because of poor electrical contact between the electrical probes and this layer, NiGe contacts were formed at the corners of 1cm x 1cm a-Ge samples.

To form nickel germanides, samples were loaded into a small furnace with flowing nitrogen gas, in a vacuum furnace or in-situ heat stage in a high vacuum X-Ray diffractometer. In the case of the furnace with only nitrogen gas flowing (no vacuum pumping), silicon substrates with titanium thin films were placed face down on the Ni films to act as oxygen getters during heat treatment to form NiGe. The effect of this was significant in reducing oxygen contamination of the NiGe films formed. (Note: the colour of the NiGe films was significantly different for samples formed with and without the presence of Ti). Figure 3.1 shows a schematic example of the formation of polycrystalline NiGe from an evaporated Ni layer on crystalline Ge (C-Ge). The figure shows that during the finite time it takes to form the germanides, the germanides forms by Ni and Ge reacting at the interface between Ni and Ge initially and subsequently at the continually moving interface between NiGe and Ni. In order for this to occur, Ni and Ge atoms must diffuse

through the existing Ni_5Ge_3 (the phase that forms first) or NiGe to get to the reaction site [12-16]. In [18] it is reported that both Ni and Ge diffuse to form NiGe but is Ni that is the dominant diffusing species by a ratio of 87:13.

Figure 3.1 Schematic showing the formation of NiGe on a crystalline germanium substrate. The figure shows that the NiGe formation occurs at the Ni and NiGe interface (initially the Ni and Ge interface). The reaction is complete when all the Ni has reacted. Ge and Ni atoms must diffuse to the reaction site for the reaction to take place.

Figure 3.2 shows a schematic of the polycrystalline nature of the NiGe layer formed when the reaction is complete. It is more representative in that it shows grain boundaries and the roughness of the bottom of the NiGe layer compared to the surface. Later it will be shown that this is also representative of NiGe on a-Ge but the bottom surface is much rougher – cross-section sample preparation is required to show this and that will be presented in the next chapter.

Figure 3.2 Schematic showing the formation of polycrystalline NiGe on a CRYSTALLINE germanium substrate. Note that the resulting NiGe is polycrystalline with a relatively smooth surface and varying depth of grains. The example shown above is for a 100 nm Ni film. The ratio of thickness NiGe to the initial Ni thickness is approximately 2.2

3.2 Atomic Force Microscopy (AFM)

Figures 3.1 to 3.6 show the surface topography of Ni as deposited on c-Ge and NiGe on c-Ge for different heat treatments. Figure 3.7 is for NiGe formed on a-Ge and is comparable to NiGe on c-Ge all other conditions being the same. The figures show that the surface variation is not significant. This was also observed in the high resolution TEM cross-section images. Similar results were obtained for the surfaces of NiGe on a-Ge. What is not shown is the roughness of the NiGe to Ge interface. Both surfaces, NiGe on c-Ge and on a-Ge have the same topography but the interfaces between NiGe and Ge are quite different and only the HRTEM cross-section imaging shows this.

Figure 3.3 100 nm Ni on c-Ge and no heat treatment. The Ni was deposited by electron beam evaporation. (Note, the initial surface of the Ge wafers had the same topography as the Ni coated Ge wafers)

Figure 3.4 100 nm Ni on c-Ge, 350 °C and 30 minutes heating. Samples were heat treated in a furnace with nitrogen flow and Ti coated polished silicon wafers were also included to getter oxygen.

Figure 3.5 100 nm Ni on c-Ge, 350 °C and 90 minutes heating.

Figure 3.6 100 nm Ni on c-Ge, 400 °C and 30minutes heating

Figure 3.7 100 nm Ni on a-Ge , 350 °C and 30minutes heating

Surface roughness measurements using AFM showed that there is little difference between the NiGe films with values between 2 and 3 nm.

3.3 Energy Dispersive X-Ray Spectroscopy (EDS)

Low energy electrons for EDS in an SEM gave stoichiometries of approximately 50% Ni and 50% Ge agreeing with EDS data of individual grains in the TEM cross-section samples for NiGe on a- and c-Ge (see following chapter). Surface analysis using EDS can lead to incorrect representation of the layer investigated if the electron beam energy is too high and counts are also obtained from the substrate below the layer being investigated. This occurred for the NiGe layers and Figures 3.8 and 3.9 demonstrate this. A beam energy of 5 keV showed that the NiGe composition was close to 50:50. Higher energies gave incorrect results. Figure 3.8 (a) and Figure 3.9 (a) show that the stoichiometry of the nickel germanide formed on a-Ge and c-Ge is approximately 50:50 Ni and Ge.

This is interesting, that stoichiometry is the same for both. Note this is a surface EDS and information is from a relatively large area, many grains and possible contributions from the substrate. The 5 keV results can be considered to be mainly from the bulk of the grains. Closer examination will be shown using high resolution TEM samples to examine individual parts of grains. The higher voltages in parts (b), (c) and (d) of both figures show the decrease in the Ni content reported. This is more significant in the a-Ge and this is likely connected to the rougher interface between the NiGe and the Ge.

EDAX ZAF Quantification (Standardless)

Element Normalized

SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
NiL	49.85	55.14	0.5136	1.0529	0.9771	1.0014
GeL	50.15	44.86	0.4123	0.9469	0.8684	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
NiL	87.36	0.00	4.63	87.36
GeL	84.18	0.00	4.72	84.18

(a)

(b)

Continued.....

(c)

(d)

Figure 3.8 Combined qualitative and quantitative analysis for 100 nm Ni on a p-type, C-Ge (400 C° for 30 min) sample using: (a) 5 keV, (b) 10 keV, (c) 15 keV, (d) 20 keV.

(a)

(b)

Continued.....

EDAX ZAF Quantification (Standardless)
 Element Normalized
 SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
GeL	62.11	57.01	0.3320	0.9657	0.5535	1.0000
NiK	37.89	42.99	0.4183	1.0597	0.9963	1.0456
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
GeL	483.19	20.89	2.07	23.13
NiK	114.53	3.04	4.18	37.69

(c)

(d)

Figure 3.9 Combined qualitative and quantitative analysis for 100 nm Ni on a p-type a-Ge (400 °C for 30 min) sample using: (a) 5 keV, (b) 10 keV, (c) 15 keV, (d) 20 keV.

3.4 X-Ray Diffraction (XRD)

XRD data reveals information on phase formation and on orientation of crystalline and polycrystalline films. Fig 3.10 from [3] is shown here to demonstrate the phases and orientations of nickel germanide. The nickel germanide phase with the lowest resistivity is NiGe.

Figure 3.10 2θ- XRD diffractograms of nickel germanides formed at various annealing temperatures. Corresponding phases and their crystallographic orientations are labelled [3].

Figure 3.10 is used as a reference to compare with data obtained for measurements for this project. In this figure it is shown that the phase Ni₅Ge₃ forms first, at the lower

temperatures used here, and the phase changes to NiGe at the higher temperatures. Throughout the literature [3-10] there is much variation in the different heat treatments used and therefore variations on the temperatures for the onset of formation of nickel germanide phases. Different heat treatment processes are used and durations of heat at particular temperatures.

Figure 3.11 shows XRD diffractograms for successive high temperature treatments of a Ni film on a crystalline germanium substrate. The data for the plots was obtained by heat treatment with in-situ XRD. The peaks for NiGe are indicated by markers at the top of the plot. Inspection of successive diffractograms indicates a continued change in the relative intensity of the 2-Theta peaks. NiGe has 2- θ peaks at 34.64° , 35.20° , 36.97° , 42.7° , 44.23° , 53.43° and 58.74° . ‘Cards’ showing the positions of relevant and likely (and some not so likely) are given in Appendix A. Card number 070297 shows the peaks for GeNi, which is the same as NiGe. The small peak at 200°C is likely to be a Ge peak as it has several peaks between 42° and 46° as listed in card 721425 in Appendix A. The XRD 2-Theta positions for other phases of Nickel Germanide are also listed in Appendix A.

2 θ - XRD diffractograms were also obtained for thicker Ni films and show that for a 400 nm film it had not fully reacted until it was heated for close to 50 minutes (the XRD scans were still changing with time). Figure 3.12 shows the XRD diffractograms for different thicknesses of Ni heated at 400°C for 60 minutes. The reaction had fully completed for each of these thicknesses. It is noted that the diffractograms all have similarly occurring peaks.

Figure 3.11 XRD diffractograms at temperatures in the range 200-400 °C for heat treatments on samples with 50 nm Ni deposited in c-Ge. Each successive temperature was held for 5 minutes.

Figure 3.12 XRD diffractograms of nickel germanides formed at various annealing temperatures and for heat duration of 60 minutes.

Figure 3.13 is a comparison of XRD diffractograms for NiGe formed on crystalline and amorphous germanium. Again it is noted that the position of peaks are remarkably similar. This is in contrast with electron diffraction images which though of the same crystal, reveal much more the polycrystalline nature of the films.

Figure 3.12 XRD diffractograms of nickel germanide formed from 50 nm Ni on crystalline and on amorphous germanium, heated for 30 minutes at 300 °C.

The results have indicated that for the minor decrease in temperature from 300 °C to 275 °C, the time of the reaction to obtain a fully formed NiGe has extended significantly. The XRD results have shown that for the heat treatments at progressively higher temperatures, the NiGe was formed at ~ 300 °C. XRD spectra and measurements of sheet resistance have both shown that minor variation in temperature above and below 275 °C has resulted in a rapid alteration in the rate of formation of NiGe. The onset of formation of NiGe occurred at ~225 °C although the completion of the reaction at this temperature was

not practical. Even with increase in temperature to 275 °C, the time duration of more than 20 hours for the complete reaction of 50 nm of Ni was impractical. The steady decrease in sheet resistance measured with time at 275 °C has been more sensitive in detecting the growth of NiGe than XRD.

In ref [17] it was reported that the mechanism for the formation of NiGe is complex and involves two germanide phases. The formation of the NiGe phase was found to begin in the temperature range from 239C-285C but here in this work it was found to begin at the slightly lower temperature of 225C. However in [17] it was determined that a different phase, Ni_5Ge_3 , formed first at approximately 145C and then the NiGe phase formed, but at the higher temperature and it remained the last phase until the end of the reaction (all the Ni being consumed and also all of the Ni_5Ge_3 phased being changed to NiGe). This is in agreement with the XRD results by Muller et al (see Figure 3.10). In [17] nickel was reported to be the sole diffusing species during the formation of the Ni_5Ge_3 phase and then there was some diffusion of Ge from the substrate during the formation of NiGe.

The Ni_5Ge_3 that formed at the lower temperatures decomposed by the mechanism $\text{Ni}_5\text{Ge}_3 \rightarrow 3\text{NiGe} + 2\text{Ni}$. The Ni that was released then reacted with Ge originating from the substrate. Ni and Ge diffused during the formation of NiGe, but Ni was the dominant diffusing species. When all the Ni is consumed the NiGe grows with a much faster rate by the consumption of Ni thermal decomposition mechanism. Simultaneous growth of Ni_5Ge_3 and NiGe was also observed by Nemouchi et al. [19], who reported a critical thickness for Ni_5Ge_3 growth of about 20 nm before the onset of the growth of the NiGe phase.

3.5 Conclusions

Surface analysis has shown that:

- The *surface of NiGe formed on both a-Ge and c-Ge is relatively smooth and suitable for integrating into a device fabrication process,*
- The stoichiometry is very close to 50:50,
- The temperature of formation has a low temperature of onset of formation but 300°C is an appropriate temperature to realise a fully reacted layer of Ni for a thickness of 50 nm in 5 minutes.
- For 400 nm Ni on crystalline germanium, 50 minutes heat duration at 300°C is required.

3.6 References

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Chapter 4

MATERIAL CHARACTERIZATION 2 – TECHNIQUES REQUIRING CROSS-SECTION PREPARATION: Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is a powerful and complex characterising technique for materials research. Sample preparation itself involves many hours of work in order to achieve samples that reveal the characteristics of the material being investigated. Here, High Resolution TEM (HRTEM) imaging is used as well as Energy Dispersive X-Ray spectroscopy, electron diffraction and elemental mapping using electron energy loss spectroscopy (EELS). Hollow cone illumination (HCI) for HRTEM imaging is also used to better show the polycrystalline grain structure. Many researchers have used TEM to investigate the formation of metal germanides on crystalline germanium [1-11]. HRTEM cross-section images are especially revealing with regard to film structure.

The lifetime of thin film conductors (e.g. NiGe formed from heating a Ni film on a Ge substrate) has been observed to depend on the mean grain size and texture of the polycrystalline film [12]. Therefore studying and understanding the mechanisms of formation affecting these aspects of grains in such a film is important. This chapter covers TEM investigation of NiGe formed by heat treatment of Ni deposited on both crystalline germanium (c-Ge) and amorphous germanium (a-Ge).

Figure 4.1 HR-TEM micrograph for fully reacted 50 nm Ni on c-Ge. The uniformity of the layer can be seen in this figure, as it shows many grains.

Figure 4.2 HR-TEM micrograph for fully reacted 50 nm Ni on c-Ge. The relative smoothness of the surface and the sharp interface between the NiGe grains and the Ge substrate can be seen here. The bottom of the grains is somewhat rounded (compared to the top) but has no sharp features.

In Figure 4.2 the grain boundaries have been highlighted to show the individual grains. The grains are distinguishable from each other because of shading change due to each grain being a different crystal orientation and the grain boundaries are also evident. (There is ‘debris’ at the top of the layer which EELS analysis shows as containing nickel, germanium and oxygen). Examination of several sections of the NiGe layer showed that the shape and size of the grains was reasonable consistent along the layer. The reason for the small variation in grain depth is due to the slight roundness caused by the grain growth mechanism. Grain growth shape characteristics are determined by the substrate [12].

Further investigation into NiGe grown on c-Ge with different level of defects may identify if crystal defects play a role in this variation. As shown in the schematic of Fig. 3.1, the NiGe grains grown by the diffusion of Ge and Ni atoms through the partly formed NiGe layer. The shape of the grains suggest that a small variation in the Ge crystal can lead to layer thickness variation likely due to the diffusivity of Ge and Ni in NiGe being different to the diffusivity of Ge atoms in Ge and Ni atoms in Ni (self-diffusivity).

Figure 4.3 HR-TEM cross-section micrograph for fully reacted 50 nm Ni on a-Ge. The non-uniformity of the implanted Ge substrate is evident, particularly when comparing with Fig.1 (the non-implanted, undamaged substrate).

The process for forming the NiGe layers was described in chapter 3. The layers resulting from NiGe layer formation on c-Ge leads to consistently repeatable results. The thickness and the electrical resistivity are repeatable for example. So too are the grain sizes and the texture of the layers. The thickness of the NiGe layer shown in the HRTEM cross-

section images of Figs. 4.1 and 4.2 are uniform with a variation of less than 10%. Figs. 4.3 and 4.4 show an NiGe layer formed on a-Ge and there is a striking difference in the texture (compared to NiGe on c-Ge).

Figure 4.4 HR-TEM cross-section micrograph for fully reacted 50 nm Ni on a-Ge. The grain boundaries have been highlighted.

Comparison of Figs. 4.1 to 4.4 shows the non-uniformity of the NiGe/a-Ge samples. The germanium region in Fig. 4.4 shows a variety of texture and it was more difficult to get a good image when working with samples like this in the TEM instrument.

Figure 4.5 HR-TEM cross-section micrographs showing increasing magnification images of the NiGe grains formed for fully reacted 50 nm Ni on c-Ge

Figure 4.6 HR-TEM cross-section micrographs showing increasing magnification images of the NiGe grains formed for fully reacted 50 nm Ni on a-Ge

Figures 4.5 and 4.6 show progressively increasing magnification of the NiGe grains formed by heat treatment of 50 nm of Ni on c-Ge and a-Ge respectively. The amorphous Ge region is apparent in Fig 4.6. At the higher magnifications the texture of the grains is clearer and the sharpness of the boundaries for the c-Ge sample is distinctly sharper than in the a-Ge sample. With regard to Fig 4.5 the image shows some variability in thickness in the NiGe layer depending on the geometry of the NiGe grains. The grains of NiGe were thinnest at the grain boundaries. The thickness of the NiGe layer was measured as $\sim 110 \pm 20$ nm or ~ 2.2 times the thickness of the initial Ni layer. There is a striking difference in the interface between the germanides and the Ge substrate. Depths of grains vary from 90 to 120 nm for the c-Ge with the narrowest depths being near the grain boundaries. Depths of grains are also narrow at grain boundaries for the NiGe on a-Ge but the depth variation was from 60 to 160 nm considering many grains.

The varying depth and grain boundaries for the NiGe grains on the c-Ge samples are clearly seen in Fig 4.5. The interface with the germanium is not as smooth as at the surface. This shape suggests a nucleation process that can be characterised as rounded and not sharp as in prismatic (or hexagonal type) grain growth. The surface smoothness was observed by TEM cross-section imaging and AFM imaging.

Hollow Cone Illumination (HCI) was used to improve the contrast in the images for NiGe formed on a-Ge as it excites more crystallites than conventional dark field illumination using a single diffracted beam or section of a diffraction ring. An objective aperture with a semiangle of 2.1 mrad was used, with excitation of the principal Bragg

reflections in the approximate range 4–8 mrad $\sim$ d-spacing 1.5–3 Å. Figures 4.7 and 4.8 are HRTEM cross-section images formed using HCI and more clearly show the individual grains of nickel germanides formed. Figure 4.6 shows that there is improved crystallinity of the “amorphous” Ge nearer the bottom of the NiGe layer and this is not apparent in the standard HRTEM images of Figs. 4.1 to 4.6. Figure 4.8 shows that HCI clearly identifies the geometry of individual grains of NiGe.

Figure 4.7 HRTEM cross-section image obtained using hollow cone illumination. There is evidence of elementalization in the implanted Ge region below the NiGe grains.

The growth of NiGe grains is interesting to compare considering that the same polycrystalline layer is being compared on two substrates that are very different in their crystallinity, one being near perfect crystalline and the other being amorphous. In reference [13] there is much discussion and modelling work presented for texture development in polycrystalline films growing on amorphous substrates. As noted in that paper, the properties and texture of polycrystalline layers depends strongly on the microstructure and crystalline orientation of the substrate used. In the NiGe films grown in this work, those on crystalline Ge had more flat –though slightly rounded bottom interfaces but flat surfaces.

The NiGe films grown on amorphous Ge had flat surfaces again but had significant occurrences of grains that had bottom interfaces that were prismatic (‘hexagonal’) in shape. This is in agreement with the model presented in reference [13] (see Figures 4.9 and 4.10) except that the grains formed here are not ‘hexagonal’ at the top as well as the bottom. However the work presented in [13] concerned nucleation and growth of films as materials was being deposited.

Figure 4.8 HCl cross-section HRTEM image more clearly shows the geometry of the NiGe grains formed

Figure 4.9 Section of a growing single crystal on an amorphous substrate showing the different growth rates of different faces for a film grown by deposition (modified from ref [13]).

Figure 4.10 Sequence of the nucleation and texture formation in a polycrystalline film grown by deposition onto an amorphous substrate (modified from ref [13]). t_1 , t_2 , t_3 are growth duration and $t_1 < t_2 < t_3$. The web type lines in the top figures indicate the boundary of the growth of crystal layers in particular directions as demonstrated in ref [13] for the model developed.

Figure 4.11 NiGe from Ni on a-Ge growth model developed here, from ref [13]. This model is appropriate for polycrystalline films formed by heat treatment of an already deposited layer (e.g. Ni) on an amorphous substrate (e.g. a-Ge).

Figure 4.12 HRTEM cross section images adapted from Fig 4.6. The suggested growth directions are indicated with the 'web' lines indicating successive stages of growth.

In Figures 4.11 and 4.12 a suggested model for growth of NiGe polycrystalline layers on a-Ge is shown. The direction of growth is shown as into the substrate. A smooth surface results which likely results from Ni being the main atom that diffuses to the reaction site [14]. The initial Ni surface is indicated in Figure 4.12. The model shows that

there is initial nucleation at different sites and the a-Ge substrate causes hexagonal grain growth at the bottom of the grain. The orientation of the top of the grain is not affected by the a-Ge. The model for grain growth of the NiGe on c-Ge will again involve nucleation but will not lead to uniform growth in all directions. The prismatic ('hexagonal') shaped interface between the NiGe grains and the a-Ge region (as seen in Figure 4.12) does not always occur. Several adjacent grains may have this regular pattern and then several more show rough and random shaped interfaces. The reason for this is unknown but may be due to variation in substrate defects or variation in the degree of crystallinity or amorphisation.

The average size of the grains on the crystalline and amorphous substrates is very similar and as indicated in chapter 5, the electrical resistivity is the same though the growth rate, qualitatively obtained through electrical sheet resistance measurement results, is quicker for the NiGe formed on amorphous Ge. The growth of grains in a polycrystalline film is limited by the available space (here a flat surface) and constrained by the growth of adjacent crystals. As the grains connect, grain boundaries develop and have characteristic straight lines as two grains typically meet at the same lateral positions as grains grow deeper into the substrate. In ref [14] it was shown that the growth of Ni_5Ge_3 was observed to begin around 145C (see also [5]). It was followed by NiGe growth at 285C. The two phases then grew simultaneously for a short period. The Ni_5Ge_3 phase grew steadily from its onset around 145C to around 300C. Also shown in [14] is that the growth rate of NiGe is low when it grows simultaneously with Ni_5Ge_3 in the presence of unreacted Ni. When all the Ni is consumed the NiGe grows with a much faster rate by the consumption of Ni_5Ge_3 by its thermal decomposition into NiGe. In ref [15] the simultaneous growth of Ni_5Ge_3 and

NiGe was also observed and this work also reported a critical thickness for Ni_5Ge_3 growth of about 20 nm before the onset of the growth of the NiGe phase.

4.1 Electron Diffraction

Fig. 4.13 shows electron diffraction patterns for two NiGe grains formed on c-Ge. (The electron diffraction pattern for the c-Ge substrate is also shown for reference). The high degree of crystallinity is apparent. As indicated by the two NiGe diffraction patterns, there is some difference in the level of crystallinity with one grain showing a very high degree of crystallinity. The poorer pattern may be due to multiple grains affecting the pattern. Overall, analysis of several grains showed that many grains are indeed single crystal and the reason for some grains showing poorer images is likely due to the cause suggested above (overlapping of grains in the polishing process. It is highly unlikely that the thinned samples will be consisting of only one grain or part of one grain along its length).

Fig. 4.14 shows much poorer crystallinity occurs for the NiGe film formed on a-Ge. In this figure the electron diffraction patterns for regions in the NiGe on a-Ge sample and the contrast between samples is significant. There are no grains which have a level of crystallinity as good as any grain formed on c-Ge. The grains of NiGe on crystalline and amorphous Ge are similar in their orientation and this is consistent with the discussion on grain growth in reference [13]. The shape of grains is very much affected by the substrate but the orientation of the grains appears not to be. The results presented in this thesis indicate that the substrate has a bigger influence on shape than on the orientation of the grains. It cannot be doubted that the degree of crystallinity of the polycrystalline NiGe layer is determined by the substrate.

Figure 4.13. Three images of electron diffraction patterns of regions in a NiGe on c-Ge sample. On the top left hand side is the image from the Ge substrate (region 10110960). The other diffraction patterns are of different NiGe grains (10110961 and 10110962).

Figure 4.14 Electron diffraction patterns of regions in a NiGe on a-Ge sample. The a-Ge image (103lement '10110834') shows that this region is polycrystalline (rings are evident)

4.2 Elemental Mapping

Elemental Mapping was undertaken using electron energy loss spectroscopy (EELS). The results obtained were compared with the NiGe polycrystalline structure. Elemental mapping is a very useful tool, not just for identifying where elements are located but also in this case, to demonstrate the location of grains. For the NiGe/c-Ge this is quite obvious from the clarity of the HRTEM cross-section image as shown in Figure 4.15 (a). However, for the NiGe/a-Ge the clarity of the HRTEM image is not as good because of the texturing of the a-Ge region in the image obtained and the lack of clarity on where the interface between the rougher NiGe grains and the a-Ge occurs. Elemental mapping clarifies the location of the interface.

Figure 4.15 (a) HRTEM cross-sectional image of NiGe formed on c-Ge at 400 °C for 10 minutes. (b) Ni map showing the distinct distribution of Ni following the geometry of the NiGe grain given in the rectangular region outlined in (a).

(2)

(b)

As Figure 4.15 (a) and (b) show, there was no evidence of Ni below the NiGe/c-Ge interface. However, traces of Ni were present in the 'debris' above the NiGe layer as a likely result of the sample preparation process. The box outlined in Fig. 4.15 (a) indicates the region of the Ni map shown in Fig.4.11 (b). As is expected the sharpness of the Ni elemental mapping is almost as sharp as the bottom grain boundaries. Fig. 4.16 (a) and (b) show elemental mapping of Ni and Ge side by side for comparison. The level of brightness indicates the level of element composition and Ge can be seen to give more brightness in the substrate region compared to the NiGe region, as expected (Figure 4.16 (b)). In Figure 4.16 (a) the substrate is dark indicating the absence of Ni in that region. The shading in Fig 4.16 (a) and (b) clearly shows that the distribution of Ni and Ge follow the NiGe structure similar to the HRTEM cross-section imaging showing the NiGe grain shapes.

Oxygen was also included in the elemental mapping as it was a likely impurity. There was evidence of a concentration of Oxygen at the surface but it was likely to have resulted from sample preparation for analysis by TEM. There is no occurrence of oxygen in the substrate or within the NiGe layer as shown by the two images Figure 4.16 (c) and (d) which are at different magnifications.

Figures 4.16 (e) and (f) show a region of higher magnification and the mapping of Ni and Ge. Again there is evidence of debris above the grain surfaces with the occurrence of both Ni and Ge in this 'debris' layer. The crystallinity of this layer has not been determined but Figure 4.16 (d) indicates that oxygen also occurs in this layer and it may be an oxide

material composed of these three elements, broken away from the surface during the sample preparation polishing process.

Figure 4.16 Ni, Ge and O elemental mapping using a HRTEM NiGe-c-Ge sample at different magnification (a) Ni, (b) Ge, (c) O, (d) O, (e) Ni, (f) Ge.

Figure 4.17 Ni, Ge and O elemental mapping using a HRTEM NiGe-a-Ge sample at different magnification (a) Ni, (b) Ge, (c) Ni remapped, (d) O, (e) O at higher magnification image.

Figure 4.17 shows a much more varied distribution of elements but again the elemental mapping of Ni and Ge follows the polycrystalline layer structure of the NiGe layer. However, compared to the HRTEM cross-section image of the same region shown in Figure 4.6 (d) the lack of clarity in that image for what is NiGe and what is a-Ge in the interface region between the NiGe layer and the a-Ge substrate, the distinction is much clearer using the mapping of Ni and Ge to demonstrate the exact interface.

The mapping of oxygen again shows that it is present at the surface and that a separate layer has formed. Again, this may well be the result of an oxide layer having formed and breaking off during TEM sample preparation. When the heat treatment of the Ni deposited on the Ge substrates occurred, the complete elimination of oxygen from the reaction chamber was impossible and some oxide formation is highly likely.

Of significant interest in Figure 4.12 (a) and (c) is the occurrence of Ni in the amorphous germanium substrate. This is not observed in the Ni mapping of the NiGe/c-Ge samples. Ni mapping is shown twice for the same region at the same magnification. There is some slight variation between the Ni distribution in the a-Ge region as shown in Figure 4.17 (a) and (c) but the result is effectively the same. Ni has diffused into the a-Ge substrate and has formed clusters of Ni rich regions.

Repeating the imaging gives practically the same mapping results. The localised effect of this on the material properties at the cluster locations has not been determined but is likely to cause local variation in electrical conductivity. Elemental mapping has shown

new information not apparent in the HRTEM cross-section imaging. This is demonstrated by the comparison of images shown together in Figure 4.18. It is striking that there is the occurrence of Ni clusters at significant depths below the NiGe grains. The migration of Ni deep into the a-Ge (and the non-migration of Ni atoms into the c-Ge) suggests the complex mechanisms that are occurring during heat treatment to form NiGe on a-Ge. In [14], Habanyam et al indicate that the formation of NiGe on c-Ge is a complex process compared to the formation of NiSi on c-Si and results here suggest that the formation of NiGe on a-Ge is even more complex.

Figure 4.18 HRTEM cross-section image of region of NiGe/a-Ge and two corresponding Ni maps of the same region. The images indicate that there is no obvious connection between features in the region of the a-Ge and the clusters observed in the Ni maps.

4.3 Energy Dispersive X-Ray Spectroscopy (EDS)

EDS is a very useful and convenient technique for determining element composition. It does not have the resolution of x-ray photon spectroscopy (XPS) but is much more convenient to use. In the examples examined here, EDS is localised to small regions of the cross-section samples and this is an excellent way to identify elements in thin films and any occurrence of migrated elements. EDS was available as a tool in the TEM system used. Regions of samples examined were the NiGe and the Ge substrate regions of c-Ge and a-Ge. Elements identified included Ni, Ge and oxygen. The peak heights give information of relative composition, e.g. NiGe desired should have approximately 50:50 composition and peak heights are approximately the same.

In the figures shown here there are labels on the relevant high resolution TEM images and these, particularly for the polycrystalline NiGe regions identify which grain and approximate position in the grain that is being examined. The technique is useful to compare with the elemental mapping done using the HRTEM images shown earlier in this chapter. The regularity and uniformity of the NiGe on c-Ge and the c-Ge itself are again observed. For EDS spectra obtained using the TEM samples, higher energy peaks are compared. This is unlike the EDS spectra obtained using SEM samples. Higher energy electron beams could not be used as Ge counts were inaccurate at high beam energies, with counts for Ge also coming from the substrate as well as the NiGe layer.

The counts obtained in the EDS spectra using the TEM samples are therefore more accurate, representative of the NiGe layer only or Ge substrate, whichever the case.

Figure 4.19 EDS qualitative results for fully reacted 50 nm Ni/c-Ge. The results are for areas sp1, sp2, sp3, sp4, and sp5. Markers for peaks are shown in the top spectra.

Figure 4.19 indicates that NiGe grains have similar composition of Ni and Ge with sp² showing some oxygen contamination. Sp³ (c-Ge region) is as expected with large Ge peaks. Ni appears as the main element in the debris layer with a significant amount of oxygen also occurring (sp⁴ and sp⁵).

EDS spectra were also obtained for other NiGe thicknesses and similar peak ratios were observed. However, it was more difficult to obtain true EDS spectra for layers that were not thinned as TEM samples, such as the samples discussed in chapter 3, and the Ge peaks were affected by the substrate. However, in that case, using low energy electron beams and NiGe layers that were estimated to be approximately 400 nm to 1000 nm, the peak ratios were similar. There is no such problem with doing EDS with thinned cross-section samples and the region examined is localized and there is only the one 'layer' that is being characterized, the electron beam does not interact with another material other than the one it is localized on.

For the HRTEM samples, higher energies could be used to obtain EDA data. This can be seen comparing the EDS data plotted in Figure 3.8 of chapter 3 for example. This will allow more accurate EDS analysis. In the HRTEM cross-section the EDS data shown in Figures 4.19 to 4.22 all have high energy peaks and these peaks are more reliable and easier to compare than lower energy peaks (the only reliable peaks in EDS data obtained using SEM samples, see chapter3).

Analysis of the EDS data for NiGe grains, whether on c-Ge or a-Ge, gave approximately 50:50 compositions for all grains. This composition was also obtained for samples examined using EDS in an SEM, with samples that were prepared as standard SEM samples (little preparation required compared to HRTEM cross-section samples). It is remarkable that the NiGe grains on a-Ge are shown to have 50:50 stoichiometries (and near ideal resistivity also – shown in chapter 5). It is remarkable considering the different structure of the grains i.e. the rougher bottom interface suggesting non-uniformity in the reaction rates and growth of NiGe grains from what was a uniform thickness and uniform composition Ni evaporated layer. The HRTEM images do show that the order of the dimensions of the grains (NiGe on c-Ge and a-Ge) are very similar, indicating that the growth mechanism is similar. Figure 4.19 indicates that there is no oxygen present in the c-Ge substrate and also none in one NiGe grains examined and possibly a small amount in another grain that was examined closer to the surface. There is significant amount of oxygen, nickel and germanium in the ‘debris’ layer evident above the NiGe. This may well be an oxide that formed during heat treatment and has broken off during TEM sample preparation and is embedded in the glue used in this preparation

Fig 4.20 – 4.22 show EDS peaks for certain regions of NiGe formed on a-Ge. There are many regions of interest here and several more figures than for the NiGe on c-Ge. Of significant importance is that the EDS spectra are very similar for NiGe grains when comparing NiGe/c-Ge in Figure 4.19 (a) and (b) with 4.20 (b). On the c-Ge different grains give almost identical EDS spectra and for NiGe/a-Ge the EDS spectra is almost identical to those for NiGe/c-Ge. However there are some grains in the NiGe/a-Ge which give slightly

different EDS spectra, but not significantly so. The stoichiometry was always close to 50:50 for NiGe/c-Ge and for NiGe/a-Ge the stoichiometry varied from approximately 48:52 to approximately 50:50. There is no doubt that uniform NiGe/c-Ge layers can be more reliably and routinely formed.

Figure 4.20 EDS qualitative results for fully reacted 50 nm Ni/a-Ge. The results are for areas sp1, sp2, sp3 and sp4.

Figure 4.21 EDS qualitative results for fully reacted 50 nm Ni/a-Ge. The results are for areas sp5, sp6, sp7 and sp8.

Figure 4.22 EDS qualitative results for fully reacted 50 nm Ni/a-Ge. The results are for areas sp9, sp10 and sp11.

For the nickel clusters identified and shown in Figure 4.18, it was not possible to identify these in the HRTEM cross-section images used for EDS of localized regions. If it were, then further evidence would be obtained of the Ni content, i.e. further evidence of the remarkable occurrence of Ni relatively deep into the a-Ge substrate.

Examination of figures 4.20 to 4.22 shows that there is no oxygen present in the a-Ge substrate but there is oxygen present in the NiGe grains. Considering the amount indicated, this is no more than in the NiGe grains formed on c-Ge.

4.4 Discussion

The structure of nickel germanide formed on amorphous or crystalline germanium has been revealed by TEM analysis. The instrument used for TEM analysis has many features including High Resolution TEM (HRTEM) imaging which gives excellent cross-sectional images of the thin films investigated. Particularly revealing is the depth of the films, the surface and bottom interface texture (which is strikingly different for the NiGe formed on a-Ge compared to that on c-Ge), and the grain dimensions and shapes. Of particular interest was the atomic structure shown in HRTEM cross-section images and these show the crystallinity of the formed NiGe grains and the transition over a short distance from the crystalline Ge to the crystalline NiGe grains. The sharp transition from the c-Ge to the NiGe is particularly revealing.

It can be assumed that this sharp interface will lead to better quality (lower resistance) ohmic contacts. With the TEM instrument used there were additional analysis tools available and these included Energy Dispersive X-ray analysis of particular regions (of a few nanometres in dimensions) of the sample cross-sections for element composition, elemental mapping over the whole cross-section imaged area, hollow-cone illumination to more clearly reveal the grain boundaries, and of course electron diffraction patterns at particular spots of the samples. Electron diffraction patterns reveal the quality of the NiGe grains formed, whether they are single crystal grains or not and electron diffraction also shows the elemental composition of the 'a-Ge' after the heat treatment used to form the NiGe layer.

4.5 Conclusion

The structure of nickel germanide formed on amorphous or crystalline germanium has been examined by TEM analysis. Results show that the texture of the bottom interface of the polycrystalline NiGe layers is different but the top surface is similar. NiGe grains on c-Ge are relatively smooth at top and bottom but the bottom of the NiGe grains on a-Ge is rough and often has a shape of a 'hexagonal grain', though this is not consistent. Why the grains are not hexagonal at both top and bottom is unknown. The NiGe grains on c-Ge are much more uniform through the NiGe/c-Ge layers formed.

Electron diffraction results show that the substrate crystallinity does not determine the orientation in the growth of NiGe on germanium though it does determine the degree of crystallinity of the grains formed and from EDS results the amorphous substrate certainly leads to less uniformity in composition of grains, though not significantly so.

There are several issues for further investigation (beyond the scope of this project):

Why does the near perfect prismatic growth occur along several adjacent grains and then go to rough random shapes? One possible investigation would be to use higher doses and energies and this may reveal more or less prismatic interface between the NiGe and a-Ge

1. Determining the source for formation of the 'debris' which may well be an 'oxide' layer. This layer is shown in the cross-section HRTEM images and EELS elemental mapping.

2. Why do clusters of Ni form deep into the a-Ge? This is a surprise occurrence, observed by EELS mapping. Further investigation is important in order for the amorphisation process and the NiGe formation to be both integrated into semiconductor device processing.

4.6 References

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Chapter 5

ELECTRICAL CHARACTERIZATION OF c-Ge and a-Ge

5.1 Introduction

Nickel germanide formed on amorphous and crystalline germanium was investigated for sheet resistance, resistivity and specific contact resistivity of Al to the NiGe layers. Gaudet et al has presented a significant report [1] on the electrical characterization of metal germanides on c-Ge and many other researchers have reported on metal germanide for use in CMOS technology [2-18]. Gaudet et al [1] identified NiGe as the lowest resistivity phase of nickel germanide. This chapter reports on electrical characterization of NiGe using both c-Ge and a-Ge. Electrical characterization is essential to determine the suitability of the processing used to form the germanides, in particular the amorphisation. Reduction in dopant diffusion is an advantage of amorphisation [19] but this has to come with a suitably low sheet resistance (for the

germanide layer formed) and ohmic contact formation to the germanide that has suitably low contact resistance and is reliable.

5.2 Materials and Method

Sheet resistance values were determined using the four-point probe technique and specific contact resistance was determined using the cross Kelvin resistor structure extrapolation method [17]. The four point probe technique with a dedicated test setup is convenient to use for large area and small area samples but correction factor must be appropriate for the sample used. The correction factor is well established for large area samples. Figure 5.1 demonstrates how the appropriate correction factor was determined for small samples. Germanium is a relatively expensive substrate and every effort was made to use the material to best advantage. In Figure 5.1 the top schematic shows the standard four point probe set up where the thin film on a 2 inch wafer is much wider than the probe spacing. (Note the thin film thickness should also be much thinner than the probe spacing, which is standard, in order to use the equation shown). The bottom setup is more practical when substrates are expensive and many samples are used. Having the same sheet resistance in the top and bottom samples, the proportionality factor can be obtained and it will be less than 4.54. The same factor can be used for testing subsequent heat treatment effects on the same sample. An alternative to this is to use published correction factors such as those published by the author in [18].

Figure 5.1 Four point probe arrangements and equation for different probe spacing compared to sample size.

Samples used were typically 1cm x 1cm. Computer modeling to obtain the appropriate correction factor was run to check the values used [18]. A paper on this computer modeling is presented in the appendix to this thesis. The resistivity of the substrate in the case of the c-Ge and the a-Ge was appropriately high in both cases such

that the electrical current could all be assumed to flow in the Ni or NiGe layers formed. To be correct it should be stated that some layers were partially formed when tested and hence can be written as Ni+NiGe layers, as a finite amount of time is required to fully react the Ni deposited. The amount of Ni is a limiting factor in the reaction in that when it is used up, no more arrives (but there is plenty of Ge). Hence we see the bottoming out of the sheet resistance plots with time at particular heat treatment temperatures. The higher the temperature the quicker this bottoming out occurs. Another limiting factor is temperature. As temperature increases the bottoming out occurs earlier for particular Ni thicknesses. However in this study there is another factor to be considered and that is whether the substrate has had an amorphization process or not and results show that this has real effects on sheet resistance itself and on sheet resistance versus temperature and time duration of heat treatment. Sheet resistance values were also determined and confirmed using the Van der Pauw technique.

The preparation of samples was the same for all Ni thicknesses investigated and this process, which involves Ge substrate cleaning, Ni evaporation and heat treatment, is described in the previous chapter (section 3.1 of Chapter 3).

A dedicated, commercial four-point probe setup was used for larger samples and for smaller samples. Micromanipulators were used for both the four-point probe and the Van der Pauw technique. The samples were heat treated in a furnace with a nitrogen rich environment.

5.3 Results

Figure 5.2 shows that the thickness of Ni affects the reaction time for the formation of NiGe. It is understandable that the thicker Ni will take longer to react fully and it is interesting to observe that for the thicknesses used the influence of several minutes at the temperatures used is significant. It becomes apparent that both temperature and heat duration time are important factors in germanides formation. In 5 minutes at 400 °C it is apparent that the 200 nm and the 400 nm Ni films have not fully reacted.

Focusing on the initial Ni thickness of 50 nm it is interesting to note that these results have indicated that at 300 °C, the reaction of the Ni and c-Ge was complete with the sheet resistance reaching a minimum value of 1.5 Ω per square in ~1 minute. The results have indicated that it was possible to form NiGe at 275 °C but that a relatively long time was required for completion. This result has differed somewhat from the XRD data since after 5 minutes the XRD data has suggested that the formation of NiGe was complete. However, a close inspection of successive diffractograms has indicated a continued change in the relative intensity of the 2-Theta peaks. The results have indicated that for the minor decrease in temperature from 300 °C to 275 °C, the time duration of the reaction to obtain a fully formed NiGe has extended significantly.

Figure 5.2 Sheet Resistance versus temperature for different thicknesses of Ni on crystalline Ge (c-Ge) for heat treatments of 5 minutes.

Figure 5.3 demonstrates the resistivity (or effective resistivity for the thicker Ni) of the NiGe formed. This figure (and also using Figure 5.2) shows that at smaller values of Ni the resistivity of the NiGe is approximately $15\mu\Omega\text{cm}$ (this is the ideal resistivity or often reported, lowest resistivity of NiGe). It is interesting to note that the initial Ni thickness of 25nm leads to a slightly higher value of resistivity compared to that of 50 nm of Ni. (NOTE: based on cross-sectional images of the NiGe films formed in this study the ratio of 2.3 (NiGe:Ni) has been used to determine the thickness of NiGe formed from fully reacted Ni.)

Figure 5.3 NiGe Resistivity versus initial Ni thickness on c-Ge for heat treatments of 5 minutes at 400 °C. Note, at 400 °C the different thicknesses of Ni were fully reacted or almost fully reacted to form NiGe and hence the resistivity values are only effective values for the thicker Ni.

Figure 5.4 is a plot of resistivity to demonstrate the longer time for complete reaction of 400 nm of Ni, but the resistivity does eventually reach that characteristic of high quality NiGe.

Figure 5.4 NiGe Resistivity versus duration of heat treatment for several heat treatments of initial Ni thickness of 400 nm on c-Ge. The values at lower duration times are really effective resistivity values and above 30 minutes the reaction is clearly complete and the true values of resistivity are determined.

Figure 5.5 demonstrates that the sheet resistance of NiGe formed on amorphised Ge does not significantly differ from that on c-Ge but it is consistently higher when fully formed. It is also interesting to note that the NiGe on a-Ge appears to fully form at slightly lower temperature, all other conditions being the same.

Figure 5.5 Sheet resistance versus temperature for different initial thicknesses of Ni on crystalline Ge (c-Ge) and amorphous Ge (a-Ge) for heat treatments of 5 minutes duration.

Figure 5.6 shows that the resistivity or effective resistivity of NiGe is usually higher on a-Ge compared to c-Ge but there is occurrence in the transition temperature region where the effective sheet resistance is lower in the amorphous germanium. This is likely due to the difference in reaction rate of the germanide formation on the a-Ge and the c-Ge.

Figure 5.6 NiGe Resistivity versus initial Ni thickness on c-Ge for heat treatments of 5 minutes at 400 °C. Note, at 400 °C the different thicknesses of Ni were fully reacted or almost fully reacted to form NiGe and hence the resistivity values are only effective values for the thicker NiGe layers investigated.

Figures 5.7 and 5.8 are plots formed from the same data. Again they show that sheet resistance (or effective resistivity) is always higher for NiGe films formed on a-Ge than on c-Ge.

Figure 5.7 NiGe Resistivity versus duration of heat treatment for several heat treatments of initial Ni thickness of 400 nm on c-Ge and a-Ge. The values at lower duration times are really effective resistivity values and above 30 minutes the reaction is clearly complete and the true values of resistivity is determined

Figure 5.8 NiGe sheet resistance versus duration of heat treatment for several heat treatments of initial Ni thickness of 400 nm on c-Ge. This figure uses actual sheet resistance measurements used in Figure 5.7 but without converting the data into resistivity or effective resistivity.

In Figure 5.7, the values at lower duration times are really effective resistivity values and above 30 minutes the reaction is clearly complete and the true values of resistivity are determined. In Figure 5.8 actual sheet resistance measurements are used, without converting the data into resistivity or effective resistivity (as in Figure 5.7). Figure 5.9 shows the interesting effect of amorphization on the formation of NiGe and in the degradation of NiGe at higher temperatures. Overall, NiGe on a-Ge has a slightly higher temperature range where it has stable values of resistivity, i.e. when the germanide formation has completed.

Figure 5.9 NiGe sheet resistance versus temperature for 5 minutes duration of heat treatment for 50 nm of initial Ni thickness on a-Ge and c-Ge

Increasing the heat duration at lower temperatures led to interesting observations. Here the focus again was on the samples with initial Ni thickness of 50 nm. The lowest temperature of complete formation of NiGe from 50 nm of Ni, determined in this study by sheet resistance measurements was 275 °C. Germanium is a relatively expensive semiconductor and many samples were used to study the formation of NiGe. The time duration required was 12 hours. At 300 °C and higher, the time required for the same formation was a matter of a few minutes. Complete formation was determined by sheet resistance measurements. At 250 °C there was insignificant change. At higher 275 °C there was a continuous decrease in sheet resistance with time until formation was complete at approximately 12 hours. No further change in sheet resistance was determined for further heat treatment.

5.4 Specific contact resistivity

In comparison with silicides for Si technology, the specific contact resistance of Al to NiGe was compared to that of Al to TiSi_2 examined in reference [17]. The same technique of extrapolating using successively small contacts to get the true value was used. The fabrication process is given in detail in [17]. This experimental work also helps to compare the level of suitability of the germanides formed on crystalline germanium to that on amorphous germanium.

The fabrication process includes Ni deposition, Ni patterning by lift-off and then NiGe formation. 100 nm of Ni was deposited by e-beam evaporation and germanide was formed by heat treatment at 400°C for 30 minutes in nitrogen with Ti coated polished silicon wafers face to face with the Ni pattern coated germanium substrates. Ti discs also included as weights on top of the Si and Ge substrates. This stack minimized oxidation of the Ni surfaces allowing the exposed and unexposed Ti surfaces to act as oxygen getters. (Eliminating or minimizing the oxidation of the nickel surface is important for forming better quality NiGe and for allowing good electrical contacts to be made with electrical probes). 100 nm of Silicon dioxide was deposited and patterned and etched slowly so as to form contact vias but remove relatively little or no NiGe material. The timing of this etching process was very important. 200 nm of aluminium was deposited by e-beam evaporation and patterned using lift-off.

Table 5.1 lists the values of specific contact resistivity were determined and clearly show that NiGe formed on c-Ge performs better in that the values are lower and more uniform with an average close to $0.8 \times 10^{-8} \Omega \text{ cm}^2$. This is lower than the average specific

contact resistivity for Al to NiGe formed on a-Ge which is close to $3.5 \times 10^{-8} \Omega \text{ cm}^2$. Considering that the International Technology Roadmap for Semiconductors requires a total effective specific contact resistivity for contacts to be less than $1 \times 10^{-8} \Omega \text{ cm}^2$ then significant improvements are required for the NiGe material especially on a-Ge and this is a likely to be the preferred process used by industry because dopant diffusion in c-Ge is such a problem in forming shallow junctions [14].

Possible reasons for the higher specific contact resistivity to NiGe (a-Ge) are that the crystal quality of the individual grains is poorer as shown in electron diffraction images in chapter 4. Improving this so the grain crystal surfaces are comparable to NiGe on c-Ge is a likely way to improvement of the specific contact resistivity. In [17] the reported values of specific contact resistivity for TiSi_2 contacts to Si were $2\text{-}4 \times 10^{-9} \Omega \text{ cm}^2$.

Table 5.1 Specific Contact Resistivity of Al to NiGe formed on c-Ge and a-Ge

Sample Number	Al to NiGe (c-Ge)	Al to NiGe (a-Ge)
	$\times 10^{-8} \Omega \text{ cm}^2$	$\times 10^{-8} \Omega \text{ cm}^2$
1	1.2	4.0
2	1.1	4.1
3	0.9	3.2
4	1.0	3.4
5	0.7	1.9
6	0.9	2.0
7	0.9	2.7
8	0.8	3.9
9	1.4	7.2
10	0.8	2.8

5.5 Conclusion

The lowest temperature of formation was 275 °C but the time for the reaction to complete was impractical at 12 hours. At 400 °C and higher, NiGe formed in a few minutes from thin films of Ni of different thicknesses on c-Ge. The effective resistivity of all NiGe formed was 15 to 17 $\mu\Omega\cdot\text{cm}$, consistently. The steady decrease in sheet resistance measured with time at 275 °C has been more sensitive in detecting the growth of NiGe than XRD.

Sheet resistance values of the NiGe films were obtained through a series of measurements and results indicate that NiGe on a-Ge has on average a 10 to 20% higher value but with considerable variation. The NiGe on a-Ge has a minimum resistivity of approximately 17 $\mu\Omega\cdot\text{cm}$. Results for specific contact resistivity of Aluminium to NiGe show that the NiGe on c-Ge performs much better and the difference is much more significant than the difference in sheet resistance between c-Ge and a-Ge. The average value obtained for Al to NiGe(c-Ge) was $0.8 \times 10^{-8} \Omega \text{ cm}^2$ and for Al to NiGe formed on a-Ge it was $3.5 \times 10^{-8} \Omega \text{ cm}^2$. Further improvements are required to lower these values in order to meet the requirements of future Ge semiconductor devices if they are to be used in high speed devices. This is likely the area where NiGe on a-Ge needs most improvement as its benefits in forming shallow junctions are significant but low contact resistance is also required.

The crystal quality of both films is similar with a slight increase in sheet resistance

for the germanide on amorphous germanium; however the greater depth of this germanide makes it less suitable for shallow junctions. The NiGe on c-Ge has a minimum resistivity of $15\mu\Omega\text{cm}$ when fully reacted, whereas the minimum achieved with a-Ge was $17\mu\Omega\text{cm}$. This is remarkable in the little difference between the two values considering the significant texture difference of the polycrystalline structure of both films. The a-Ge and the c-Ge behaved differently in regard to reaction times and the effect of high temperature. The a-Ge was quicker to react and fully form nickel germanides and slower to degrade with higher temperatures that increased the sheet resistance, degrading the NiGe films. The NiGe films in both cases had a stable temperature range of about 200C, from 300C to approximately 500C. The c-Ge material could easily be probed electrically but good ohmic contacts using NiGe had to be made to the a-Ge layer in order to undertake electrical measurements on it, to consider its effect on NiGe sheet resistance. However the results were not quantifiable other than to state that the sheet resistance was much higher than could be accurately and reliably determined. The amorphization process increases the resistivity of the germanium significantly in the amorphised region.

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Chapter 6

Conclusions

There is significant interest in germanium for semiconductor devices due to the very high electron and hole mobilities that are possible in germanium compared to silicon [1]. Incorporation of germanium into CMOS technology is being pursued [1-3] and this has occurred through the introduction of high permittivity (high- κ) materials for the gate dielectric in standard CMOS processing and the shift away from silicon/silicon dioxide structures. New materials are being considered for devices and germanium is attractive because of higher mobilities and is relatively compatible with current CMOS technology. The International Technology Roadmap for Semiconductors (ITRS) 2013 edition states that for <10 nm technology the introduction and heterointegration of high mobility channels based on III-V materials and Ge are solutions, to replace strained Si for continual

performance. The same source also states that for continual Effective Oxide Thickness (EOT) scaling, using Ge and III-V semiconductors can also lead to possible solutions. However, there are still key challenges to be overcome before the full potential of germanium MOS devices can be realised and among these is the issue of reliable ohmic contacts. Like silicides (e.g. NiSi) for low resistance contacts for silicon technology, germanides (e.g. NiGe) are suitable for germanium technology.

Germanides are conveniently formed by heating a metal layer on germanium. Many metals form germanides this way and nickel germanide in the form of NiGe is advantageous for use in germanium semiconductor devices as it has a low resistivity comparable to that of NiSi which is a well-known electrical contact material in silicon devices. Other forms of nickel germanide, other than NiGe, are not desirable as they have higher resistivities. However, NiGe conveniently forms at temperatures of 400C and lower. This thesis reports on the thermal budget required to form NiGe on n and p-type germanium at low temperatures (less than 400C) and reports on the temperature duration required for fully reacting Ni of different thicknesses to form NiGe.

The formation of nickel germanide has been examined over a range of low temperatures (200-400 °C) in an attempt to minimize the thermal budget for the process. Cross-sectional Transmission Electron Microscopy (TEM) was used to determine the texture of the germanide layer and the morphology and constituent composition of the Ge/NiGe interface. The onset and completion of reaction between Ni and Ge were

identified by means of a heated stage in combination with in-situ x-ray diffraction (XRD) measurements. The stages of reaction were also monitored using measurements of sheet resistance of the germanides by the Van der Pauw technique. The results have shown that the minimum temperature for the initiation of reaction of Ni and Ge to form NiGe was 225 °C. However, an annealing temperature ≥ 275 °C was necessary for the extensive (and practical) formation of NiGe. Between 200 and 300 °C, the duration of annealing required for the formation of NiGe was significantly longer than at higher temperatures. The stoichiometry of the germanide was very close to NiGe (1:1) as determined using energy dispersive spectroscopy (EDS) with only NiGe on amorphous germanium varying to as much as 48:50.

6.1 Future Work

In chapter 4 it was shown that NiGe grain growth on a-Ge was often regular in shape (prismatic) for several adjacent grains but random and rough shaped adjacent grains also occurred. Further investigation into NiGe grown on c-Ge with different level of defects may identify if crystal defects play a role in this variation. This may give insight into the question as to why does the perfect prismatic growth occur along several adjacent grains and then go to rough random shapes. Another possible investigation in this regard would be to use higher doses and energies and this may reveal more or less prismatic interface between the NiGe and a-Ge

In the High Resolution TEM cross section images of NiGe on germanium, a 'debris' layer was evident in all images. Determining the source for formation of the 'debris', which may well be an 'oxide' layer. This layer is shown in the cross-section HRTEM images and EELS elemental mapping. Identify and then possibly eliminating this layer if necessary may well improve electrical contact to the NiGe layers formed in the same manner as described in this thesis.

Another area identified for future investigation in this thesis is why do clusters of Ni form deep into the a-Ge? This is a surprise occurrence, observed by EELS mapping in chapter 4. Further investigation is important in order for the amorphisation process and the NiGe formation to be both integrated into semiconductor device processing. As stated in [4], Metals are notorious lifetime killers in silicon and germanium.

6.2 References

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Appendix-A

Powder Diffraction Files (PDF) for materials of interest for this project. PDF's are prepared by The International centre for Diffraction data (ICDD), www.icdd.com. Note the height of the lines at a particular 2θ position correspond to intensity of a particular hkl plane in a powder of the sample.

PDF # 240452, Wavelength = 1.5418 (Å)

24-0452 Quality:
 CAS Number:
 Molecular Weight: 189.99
 Volume[CD]: 142.09
 Dx: 8.881 Dm:
 Sys: Orthorhombic
 Lattice: Primitive
 S.G.: Pnma (62)
 Cell Parameters:
 a 5.11 b 3.83 c 7.26
 α β γ
 SS/FOM: F30=10(0.083, 37)
 I/Cor:
 Rad: CuK α
 Lambda: 1.5418
 Filter:
 d-sp: Guinier

Ge Ni2
 Germanium Nickel
 Ref: Elner et al., J. Less-Common Met., 24, 23 (1971)

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
26.289	10	0	1	1	47.794	80	1	1	3	60.774	20	3	1	1
30.140	40	1	0	2	49.654	5	2	1	2	62.688	50	2	0	4
31.535	5	1	1	1	50.150	10	0	0	4	64.634	40	1	2	3
35.080	40	2	0	0	51.954	60	2	0	3	65.090	5	3	1	2
38.385	60	1	1	2	53.491	5	1	0	4	66.128	60	2	2	2
41.221	60	1	0	3	55.306	20	3	0	1	66.876	40	1	0	5
42.416	80	2	1	0	57.256	20	1	2	2	69.118	5	0	1	5
43.203	65	2	0	2	57.687	50	2	1	3	71.529	5	0	2	4
44.224	100	0	1	3	59.063	20	1	1	4	71.844	10	1	1	5
44.361	100	2	1	1	59.906	40	3	0	2	73.001	50	2	2	3
47.371	85	0	2	0	60.337	20	2	2	0					

PDF # 351359, Wavelength = 1.54060 (Å)

35-1359 Quality: *
 CAS Number:
 Molecular Weight: 248.69
 Volume[CD]: 45.62
 Dx: 9.053 Dm:
 Sys: Cubic
 Lattice: Primitive
 S.G.: Pm3m (221)
 Cell Parameters:
 a 3.573 b c
 α β γ
 SS/FOM: F13=45(0.171, 17)
 I/Cor:
 Rad: CuK α 1
 Lambda: 1.54060
 Filter: Ni
 d-sp: diffractometer

Ni3 Ge
 Germanium Nickel
 Ref: Cannon, J., Humphreys, Brigham Young University, Provo, Utah, USA, ICDD Grant-in-Aid

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
24.928	3	1	0	0	75.178	22	2	2	0	119.17	4	4	0	0
35.535	3	1	1	0	80.572	1	2	2	1	125.43	2	4	1	0
43.856	100	1	1	1	91.302	21	3	1	1	140.01	16	3	3	1
51.091	42	2	0	0	96.636	7	2	2	2					
63.756	2	2	1	1	102.01	1	3	2	0					

PDF # 040545, Wavelength = 1.5405 (Å)

04-0545 Quality: *
 CAS Number: 7440-56-4
 Molecular Weight: 72.59
 Volume[CD]: 181.09
 Dx: 5.325 Dm:
 Sys: Cubic
 Lattice: Face-centered
 S.G.: Fd3m (227)
 Cell Parameters:
 a 5.657 b c
 α β γ
 SS/FDM: F13=67(.0121, 16)
 I/Cor:
 Rad: CuKα1
 Lambda: 1.5405
 Filter: Ni
 d-sp:

Ge
 Germanium
 Ref: Swanson, Tatge, Natl. Bur. Stand. (U.S.), Circ. 539, I, 18 (1951)

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
27.282	100	1	1	1	83.681	17	4	2	2	126.43	4	5	3	3
45.303	57	2	2	0	90.052	7	5	1	1	141.20	2	4	4	4
53.679	39	3	1	1	100.75	3	4	4	0	152.90	8	5	5	1
66.013	7	4	0	0	107.32	11	5	3	1					
72.799	10	3	3	1	118.85	6	6	2	0					

PDF # 882326, Wavelength = 1.54060 (Å)

88-2326 Quality: C
 CAS Number:
 Molecular Weight: 58.70
 Volume[CD]: 41.06
 Dx: 9.495 Dm: 8.900
 Sys: Cubic
 Lattice: Face-centered
 S.G.: Fm3m (225)
 Cell Parameters:
 a 3.45 b c
 α β γ
 I/Cor: 7.34
 Rad: CuKα1
 Lambda: 1.54060
 Filter:
 d-sp: calculated
 ICSD #: 041508

Ni
 Nickel
 Ref: Calculated from ICSD using POWD-12++
 Ref: Haglund, J et al., Phys. Rev. B: Condens. Matter, 48, 11685 (1993)

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
45.502	999 *	1	1	1	53.045	412	2	0	0	78.324	157	2	2	0

PDF # 721425, Wavelength = 1.54060 (Å)

72-1425 Quality: C
 CAS Number:
 Molecular Weight: 72.59
 Volume[CD]: 245.45
 Dx: 5.893 Dm: 5.860
 Sys: Tetragonal
 Lattice: Primitive
 S.G.: P4₃2₁2 (96)
 Cell Parameters:
 a 5.930 b c 6.980
 α β γ
 I/Cor: 5.33
 Rad: CuKα1
 Lambda: 1.54060
 Filter:
 d-sp: calculated
 ICSD #: 016954

Ge
 Germanium
 Ref: Calculated from ICSD using POWD-12++, (1997)
 Ref: Bundy, F.P., Kasper, J.S., Science, 139, 340 (1963)

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
19.628	53	1	0	1	55.855	91	3	2	0	75.163	52	2	0	5
21.171	4	1	1	0	57.127	1	1	1	4	76.065	1	4	0	3
24.749	202	1	1	1	57.525	13	3	2	1	76.843	1	4	2	2
29.678	456	1	0	2	59.283	1	2	2	3	77.155	9	2	1	5
32.791	999*	2	0	1	61.507	46	3	0	3	78.049	2	4	1	3
33.376	279	1	1	2	61.622	25	2	0	4	80.122	47	3	2	4
33.771	8	2	1	0	62.364	13	3	2	2	81.007	1	4	3	0
36.205	143	2	1	1	62.610	51	4	0	0	82.417	14	5	0	1
41.666	6	1	0	3	63.685	61	3	1	3	82.960	4	5	1	0
42.791	7	2	1	2	63.798	33	2	1	4	83.925	28	4	2	3
43.112	7	2	2	0	64.767	1	4	1	0	84.364	25	5	1	1
44.497	33	1	1	3	66.301	5	4	1	1	84.873	13	1	0	6
45.117	1	2	2	1	66.887	22	3	3	0	84.990	15	3	0	5
47.785	116	3	0	1	68.396	15	3	3	1	85.968	29	4	0	4
48.507	112	3	1	0	69.065	1	1	0	5	86.624	40	5	0	2
49.775	251	2	0	3	69.997	6	3	2	3	86.929	37	3	1	5
50.345	153	3	1	1	70.105	3	2	2	4	87.904	1	4	1	4
50.759	377	2	2	2	70.800	1	4	1	2	88.560	37	5	1	2
52.263	52	2	1	3	71.122	6	1	1	5	88.778	22	5	2	0
52.391	153	0	0	4	72.501	49	4	2	1	89.838	14	3	3	4
53.213	12	3	0	2	72.835	18	3	3	2					
55.591	5	3	1	2	74.169	44	3	1	4					

Appendix-B

The research papers produced during my PhD project are enclosed in Appendix B.