Formation of NiGeSn Material for Thermoelectric Applications

BEJAN HAMAWANDI

Master of Science Thesis
Stockholm, Sweden 2014

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Abstract

Group IV-based nanowires are excellent designed thermoelectric materials for high temperature applications. Ni silicide (germanide) has been widely used to reduce the contact resistance for group IV nanowires. In this work, the interaction of Ni with relaxed, compressive and tensile strained GeSn was investigated. The layers were epitaxially grown by chemical vapor deposition in temperature range 290-350 °C and the phase transformation of germanides was studied for three different rapid thermal annealing (RTA) temperatures of 350, 450, and 550 °C. The germanide layers were characterized using scanning electron microscopy, high resolution X-ray diffraction, and four point resistivity measurements. The results showed that NiGeSn phase with lowest resistivity is formed at 450 °C annealing and was stable up to 550 °C. The thermal stability of NiGeSn is dependent on the type, amount of the strain and the Sn content. The thickness of germanide layer for a certain RTA treatment was dependent on strain.
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The Aim of this work

The aim of this work is to study the formation of nickel germanium tin phase in strained (Compressive and Tensile) and relaxed structures to reduce the contact resistance for the thermoelectric device applications.
1.0 Introduction

1.1 Silicides

Silicides (or Germanides) are formed through a solid state interaction between a metal for example (Pt, Co, W, Ni) with a semiconductor; silicon, (or germanium) depending on the annealing treatment. In this work we use nickel (Ni) as a metal and Germanium-Tin (GeSn) as a semiconductor in the formation of the NiGeSn phases at different annealing temperatures as shown in figure (1).

![Figure (1) the formed Ni-silicide phases at different treating temperatures][1]

When a metal is deposited directly on a semiconductor, a potential barrier is created at the interface between the metal and the semiconductor due to the difference in the work functions of the semiconductor and metal. This formed potential barrier hinders the free movement of the electrons from and to the semiconductor as illustrated in figure (2).
Figure (2) The potential barrier when n-type semiconductor and metal are in contact. The width and height of this barrier can be designed by the choice of a metal and doping concentration in the semiconductor.

By introducing silicide between the metal and the semiconductor, the formed barrier is reduced, and it would be possible for the electrons to tunnel easily through the barrier into the semiconductor.

1.2 Silicide’s basic requirements
The silicidation process itself should not affect the device structure in terms of doping profiles and isolations. The basic requirements for metal silicides are following:[2,3]

- Low contact resistance
- Low Si or Ge consumption
- Good chemical stability in contact with the semiconductor
- Good thermal stability with the consideration of the morphology
- Feasible for Silicon process technology
1.3 Silicide and Germanide phase

The most commonly used silicide are PtSi, TiSi2, CoSi2, and NiSi [2] for the electronic devices. Table 1 shows composition and structure (Strukturbericht designation is used for comparison [4]) of refractory silicide and germanide phases of Ni, Co, Pt, and Pd. [5]

Table 1 The Silicide and Germanide phases of Ni, Co, Pt, and Pd. [5]

<table>
<thead>
<tr>
<th>Refractory metal</th>
<th>Final silicide Phase</th>
<th>Final silicide Structure</th>
<th>Final germanide Phase</th>
<th>Final germanide Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>TiSi2</td>
<td>C54</td>
<td>TiGe2</td>
<td>C49</td>
</tr>
<tr>
<td>Zirconium</td>
<td>ZrSi2</td>
<td>C49</td>
<td>ZrGe2</td>
<td>C49</td>
</tr>
<tr>
<td>Hafnium</td>
<td>HfSi2</td>
<td>C49</td>
<td>HfGe2</td>
<td>C49</td>
</tr>
<tr>
<td>Vanadium</td>
<td>VSi2</td>
<td>C40</td>
<td>VGe2</td>
<td>C40</td>
</tr>
<tr>
<td>Niobium</td>
<td>NbSi2</td>
<td>C40</td>
<td>NbGe2</td>
<td>C40</td>
</tr>
<tr>
<td>Tantalum</td>
<td>TaSi2</td>
<td>C40</td>
<td>TaGe2</td>
<td>C40</td>
</tr>
<tr>
<td>Chromium</td>
<td>CrSi2</td>
<td>C40</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>MoSi2</td>
<td>C11_b</td>
<td>MoGe2</td>
<td>C23</td>
</tr>
<tr>
<td>Tungsten</td>
<td>WSi2</td>
<td>C11_b</td>
<td>WGe2</td>
<td>C11_b</td>
</tr>
<tr>
<td>Cobalt</td>
<td>CoSi2</td>
<td>C1</td>
<td>CoGe2</td>
<td>Cc</td>
</tr>
<tr>
<td>Nickel</td>
<td>NiSi</td>
<td>B31</td>
<td>NiGe</td>
<td>B31</td>
</tr>
<tr>
<td></td>
<td>NiSi2</td>
<td>C1</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Platinum</td>
<td>Pt2Si</td>
<td>C22</td>
<td>Pt2Ge</td>
<td>C22</td>
</tr>
<tr>
<td></td>
<td>PtSi</td>
<td>B31</td>
<td>Pt2Ge</td>
<td>B31</td>
</tr>
<tr>
<td></td>
<td>PtSi2</td>
<td>B31</td>
<td>PtGe2</td>
<td>C35</td>
</tr>
<tr>
<td>Palladium</td>
<td>Pd2Si</td>
<td>C22</td>
<td>Pd2Ge</td>
<td>C22</td>
</tr>
<tr>
<td></td>
<td>PdSi</td>
<td>B31</td>
<td>PdGe</td>
<td>B31</td>
</tr>
</tbody>
</table>
1.4 Why Silicides?

In the past 50 years numerous developments were achieved in the field of semiconductor technology and it became a part of our daily life use. This is a driving force for the future industrial development and economy growth and it gives the opportunity for innovations and making new devices for different technological applications.

Silicon is the dominant semiconductor material in the semiconductor technology, it is cheap, easy to process and widely available in nature and it has good electrical and physical properties. At the present time, the microelectronic chips contain billions of devices and the structures are aggressively scaled down to nanometer (nm) scale.

The rapid down-scaling of device structures like MOSFETs (Metal-oxide-semiconductor field effect transistors) which are the building blocks for the semiconductor technology will achieve to gate lengths below 14 nm in the near future [6]. So, the contact resistance has become a very important issue for the nm-scaled devices.

The metal silicide is a solution to reduce the contact resistance at the interface between interconnect and device parts like source and drain in MOSFET. Figure (3) shows that depending on the material and the doping concentration used, it is possible to obtain different contact resistance.
Figure (3) Silicide/Si contact resistance, $R$ vs contact length, $L$ for two different interface contact resistivity.[7]

In general, silicides are promising materials to reduce the contact resistance not only for the electronic devices but also for thermoelectric components. Thermoelectric generators are green energy source and the interconnect contact resistance has a great influence on the performance of such devices. NiGeSn is a promising material for various designs of thermoelectric generators in future.

### 1.5 Nickel Silicide and Nickel Germanide

To fulfill the down-scaling requirements of the international technology roadmap for semiconductors (ITRS) [6], (NiSi) may lead the way for the future nano fabrication devices due to the integration difficulties facing the other silicide materials. For example, Cobalt-silicide has high Silicon consumption, void formation and interface roughness, and demands high temperature formation [8].
Figure (4) shows the phase diagram for the binary systems of NiSi and NiGe. The obvious difference appears in the low melting point for the germanide compared to the silicide, and the absence of the NiGe$_2$ compared with existing NiSi$_2$. The relatively low melting point for the germanide phases indicates the higher reactive diffusion in those germanide phases.

Three Ni silicide phases grow in sequence depending on the thermal treatment, starting from the Nickel rich Ni$_2$Si at low temperatures, which starts at 210°C. Then, NiSi will start growing at higher temperatures (~400°C) after a critical thickness of the Ni$_2$Si of 200 nm is achieved. Finally, NiSi$_2$ phase can be formed at temperatures higher than 700°C when enough Ni layers (50 nm) are available [9].
Figure (4) Phase diagrams for NiSi and NiGe [10]
Both binary structures NiSi and NiGe have orthorhombic crystalline structure; meaning that the lattice parameters are described as (a ≠ b ≠ c) as it is shown in table 2.

**Table 2 Physical and thermochemical properties of the silicide and germanide of Ni [3]**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Phase</th>
<th>Crystal structure</th>
<th>Lattice constant (Å)</th>
<th>T_m (K)</th>
<th>ρ (μΩcm)</th>
<th>Δh (kJ/g-atom)</th>
<th>DDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Ni₃Si</td>
<td>Cubic</td>
<td>3.504</td>
<td>-</td>
<td>-</td>
<td>1440</td>
<td>-26</td>
</tr>
<tr>
<td></td>
<td>Ni₃Ge</td>
<td>Cubic</td>
<td>3.566</td>
<td>-</td>
<td>-</td>
<td>1400</td>
<td>-25</td>
</tr>
<tr>
<td>Ni₂Si</td>
<td>Orthorhombic</td>
<td>5.00</td>
<td>3.73</td>
<td>7.04</td>
<td>1580</td>
<td>24</td>
<td>-48</td>
</tr>
<tr>
<td>Ni₂Ge</td>
<td>Orthorhombic</td>
<td>5.113</td>
<td>3.830</td>
<td>7.264</td>
<td>780</td>
<td>24</td>
<td>-37</td>
</tr>
<tr>
<td>NiSi</td>
<td>Orthorhombic</td>
<td>5.18</td>
<td>3.34</td>
<td>5.62</td>
<td>1265</td>
<td>10.5</td>
<td>-45</td>
</tr>
<tr>
<td>NiGe</td>
<td>Orthorhombic</td>
<td>5.389</td>
<td>3.438</td>
<td>5.82</td>
<td>1123</td>
<td>-32</td>
<td>Ni</td>
</tr>
<tr>
<td>NiSi₂</td>
<td>Cubic</td>
<td>5.406</td>
<td>-</td>
<td>-</td>
<td>1298</td>
<td>34</td>
<td>-31</td>
</tr>
<tr>
<td>NiGe₅</td>
<td>No existence</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The nickel silicide (NiSi) has major advantages: [2]

- Low resistivity (10-15 μΩ cm)
- Low formation temperature (~400 °C)
- Low silicon consumption

The major disadvantage for Ni-silicide in general is the poor thermal stability (melting point at 900°C) with the local contact metallization, and the creation of the high resistivity phase NiSi₂ in temperatures above 700°C. In smaller dimensions this formation may occur in much lower temperatures. As a solution, Ni can be alloyed with Pt to overcome the thermal stability. Agglomeration and morphological instability of NiSi is a major problem which creates islands at temperatures around 550-600 °C. This problem can be solved with making thinner silicide layers.[11]

In the case of the nickel germanide (NiGe), it grows in an unusual way, see figure (5). Formation starts at the annealing temperatures around 140°C and simultaneously two different phases are created, NiGe (fast growth) and then after a critical thickness of 20nm Ni₅Ge₃ (slow growth) is resulted when 50 nm Ni is accessible [9].
Nickel German-silicide, \textit{Ni(SiGe)}, is another silicide which has a better morphological stability compared to NiGe, and this may be due to the stresses introduced by the SiGe [12]. Meanwhile, increasing the concentration of Ge will decrease the thermal stability but this problem can be solved by adding carbon to the system Ni(SiGeC).[13]

1.6 Germanium – Tin

\textbf{GeSn}: Sn has 17\% lattice mismatch with Si, and 15\% lattice mismatch with Ge. Sn creates strain when it is incorporated in Si or Ge matrix. As depicted in figure (7) as Sn atoms are bigger than Ge atoms, they create a compressive strain effect on the lattice. It is important to mention that Sn has low solid solubility in Ge (1\%). It has also a low thermal stability (see the phase diagram of Sn with Ge in figure (6)). It is important to indicate that Sn tends to segregate on the surface.

\textit{Figure (5) (a) TEM and EELS analysis after an annealing at 180\_\degree C during 110 min and (b) long time collection XRD after an annealing of 50 nm Ni on a- Ge at150\_\degree C for 8 hours.}[9]

\textit{Figure (6) phase diagram of Ge with Sn.}
GeSn is grown as an epitaxial layer on a Ge substrate. The term epitaxial refers to growth of mono-crystalline layer on mono-crystalline substrate. The big Sn atoms incorporated in Ge lattice create a mismatch in the grown GeSn lattice. The GeSn thin layer deposited on Ge substrate is a design for compressive structure GeSn/Ge (see figure(7)).

Figure (7) Sn with bigger atoms creates compressive strain in the GeSn layer once deposited on Ge substrate.

The strain in GeSn alloy can be tuned by the Sn content. This can tune Ge band gap and when the Sn concentration reaches a critical percentage (~6-8%) a transition from indirect to direct band gap semiconductor may occur which is beneficial for photonic applications [14]. In terms of the mobility GeSn has higher hole and electron mobility than Si and Ge [15].
Another application for GeSn is in photovoltaics field for triple junction solar cells, as it is shown in figure (9). The Schematic diagram shows the band gap of both GeSn and SiGeSn which can be tuned by the tin content. These layers can be used as intermediate layers for the growth of III-V materials on the Si substrate to fill the large lattice mismatch between them.

Figure (8) Direct and indirect band gap values in GeSn alloy

Figure (9) Schematic diagram of the three junction design (right panel). Band gaps of group-IV alloys and III-V alloys relevant for IV/IV / III-V triple-junction solar cells. (left panel) [16]
GeSn is also a promising candidate for the thermoelectric device application. As mentioned above, the carrier mobility in GeSn is higher than Si and Ge [15], and because the mobility is related to the conductivity so theoretically these alloys may improve the dimensionless thermoelectric figure of merit ZT:

\[
ZT = \frac{\alpha^2 \sigma}{\kappa} \frac{T}{T}
\]

\(\alpha\) = Seebeck coefficient
\(\sigma\) = Electrical conductivity
\(\kappa\) = Thermal conductivity

The disorder brought by the presence of Sn is not only due to mass difference but also to the larger bonding energy as well. Sn with heavy atoms and weak bonds leads to more phonon scattering which leads to lower thermal conductivity, thus higher ZT values. For the nanowire based thermoelectric devices the thermal conductivity will be further decreased which is more beneficial for ZT.

Furthermore in this work NiGeSn material is used to reduce the contact resistance between the metallization and the nanowires in the thermoelectric device (see figure (10)). There is also the possibility to make NiGeSn nanowires to measure the thermoelectric property. An enhancement of the thermoelectric property is expected according to the effect of the Sn in Ge layer.
Figure (10) nanowires in the thermoelectric device

The NiGeSn low resistivity phase between the contact and the nanowires.
Chapter two

2.0 Experimental Work

2.1 Epitaxial growth process

Epitaxy is the deposition of crystalline layer on a crystalline substrate. The epitaxial layer is formed from dissociation of reactant gases on to the substrate at a specific temperature. The reduced pressure chemical vapor deposition (RPCVD) was used to deposit the epitaxial layer at 290-380°C. In the case of Ge and GeSn layers, the precursor gases were Ge₂H₆ (Ge source) and SnCl₄ (Sn source).

For the layer doping, Diborane (1% B₂H₆ in H₂) was used as Boron source for p-type semiconductor and phosphorous (5% PH₃ in H₂) for n-doping.

100 mm silicon (100) wafers were used in this work. Chemical cleaning of the wafers is essential to prevent any contamination by surrounding materials during the handling or packaging. A standard surface cleaning was performed prior to load to the CVD reactor. The process consists of a solution of H₂SO₄+H₂O₂+H₂O to remove particles, organics and metals, and then treated with diluted (HF) to remove the native oxides. The samples were bubbled in the de-ionized water and rinse dried.

Wafers were weighed prior and after the deposition to estimate the layer thickness.
2.2 Germanide process

Prior to the process of nickel germanide (NiGe) it is important to do another cleaning step to ensure high quality of the interface between the semiconductor (on the wafer) and the deposited metal which is Ni in this work.

It is important to note that Ge-based materials are very sensitive to water based solvents. The surface cleaning is mostly done by wet chemistry etching. As Germanium is exposed to the atmosphere two different oxides: GeO and GeO₂ are formed. GeO₂ is soluble in water and the GeO can be removed by dipping in HCl or HF. When the wafers are cleaned then they are directly transferred for Ni deposition.

Ni is deposited on the epitaxial layer GeSn using Provac PAK 600 Coating System tool. 15 nm of Ni is deposited on the GeSn under high vacuum (10⁻⁷ torr). Once the nickel is deposited on the wafer, the next important step is the rapid thermal annealing process (RTA). The RTA takes place at specific temperatures.

In this work, three different temperatures, 350, 450 and 550 °C were applied on samples, in RTA tool. Many factors determine the annealing temperatures but the most important one is enough energy to create the different phases of NiGeSn as the result of the solid state reaction between the Ni and GeSn.

2.3 RTA recipes

As it was presented in the phase diagrams the temperature range to create different nickel-germanide phases is from 200°C to 450°C. The wafers were cleaved into different pieces and annealed at 350°C, 450°C and 550°C in N₂ gas ambient.

A two-step RTA annealing method is applied for GeSn layer to obtain the germanide.

At first, a 350°C RTA is performed to create nickel rich phase, Ni₂Ge. Then the unreacted Ni on the wafers will be removed by phosphoric acid H₃PO₄ (99%) for approximately 10 minutes followed by N₂ gas purge. The nickel rich phase acts as a barrier on the top of GeSn layer and the second annealing step is performed at 450°C to create the low resistance phase NiGeSn.
The two-step annealing method is crucial if one makes GeSn nanowires, because of the fine line effect during the germanide process. As Ni atoms diffuse fast within the Ge matrix, Ni atoms will diffuse around the line structure and distort the uniformity of the wire. By removing the unreacted Ni and annealing in another step to avoid the fine line effect for the nanowires.

There are many ways to identify or characterize the created NiGeSn phases: x-ray theta-2theta scans, cross-sectional scanning electron microscope analysis, and four point resistivity measurements.
Chapter three

3.0 characterization

3.1 Scanning electron microscopy (SEM)

High resolution scanning electron microscope (HRSEM) is used to observe the surface morphology and the cross sectional image of the NiGeSn phases on the Si wafer. Both secondary electron and in lens detectors were used for the analysis. The secondary electron detection in the SEM is mainly used to image the nanowires and devices and in lens is used mainly to study the surface morphology of the epitaxial layers.

The SEM is an instrument that makes magnified images by using electron beam instead of light photons. A beam of electrons is generated at the top of the microscope by an electron gun. The electron beam accelerates and follows a vertical path through the microscope, which is in vacuum. The beam travels through electromagnetic lenses focusing it down towards the sample (see figure (11)). Once the beam hits the sample, electrons and X-rays are ejected from the sample and detected by various types of detectors [17].
3.2 High resolution x-Ray analysis

X-ray diffraction is an analytical method used to determine the crystallography structure of the sample material, phase identification for alloys, etc. It is also used to determine the lattice constant and to calculate the strain and the composition of the sample materials. The basic principle of x-ray is to detect the interference of the scattered x-ray from the different planes and measure the incident and scattered angle by the different planes to analyze the result and measure the material crystalline parameters, strain, etc.

In this project, Empyrean X-ray diffractometer was used for phase identification. theta-2theta measurements in the range of 20-110 degrees were performed. Rocking curves and reciprocal lattice mapping were also extracted for selected samples.
3.3 Four probe resistivity measurements

NiGeSn samples were annealed at 350°C, 450°C and 500°C and then measured with the four point resistivity measurement technique to identify their resistivity. The sheet resistivity of the top layer which consists of NiGeSn phase layer is measured experimentally using a "four point probe". In this technique, four probes are in contact with the silicon wafer, then a current is applied at the outer probes consequently inducing a voltage in the inner probes (see figure (12)) [18].

![Diagram of four point probe measurement](image)

*Figure (12) Use of a four point probe to measure the sheet resistivity of a NiGeSn phase layer [18]*
Chapter four

4.0 Results and discussion

4.1 SEM

Three different structures were studied in this work as shown in figure (13) with the following strain characteristics:

- Compressive strained NiGeSn
- Strain Relaxed NiGeSn
- Tensile strained NiGeSn

In the case of the compressive samples, a GeSn layer was grown on a virtual layer of Ge. Large lattice mismatch between GeSn and Ge creates compressive strain in GeSn layer. This strain can be tuned by changing the amount of Sn inside the GeSn layer.

In the case of the strain relaxed samples, a seed layer of Ge was deposited due to its difficulty to grow GeSn epitaxial layer directly on the Si substrate. On top of the Ge seed layer, it is possible to deposit a thick GeSn layer. Most of the defect is introduced to the interface due to the large mismatch between the Si substrate and the GeSn thick layer. However the top surface of the layer is free from any strain.

In general, the defect density is much higher in relaxed structures compared to the compressive GeSn structures, as thick layers introduce a high defect density in the layer.

For the tensile strained samples, two layers of GeSn with different Sn contents are grown on a substrate, the top epitaxial layer contains less Sn, therefore it involves tensile strain relative to the bottom epitaxial layer which has more tin content.
Figure (13) Summary of the three different structures for GeSn epitaxil layers

Figure (14a) shows the surface morphology for GeSn (compressive) before and after the Ni deposition and annealing in 450°C.

Before annealing the general observation is that the Sn dots are clearly noticed on the surface. By annealing the sample, Ni diffuses into the GeSn layers and the Sn dots impede the Ni diffusion (see figure (15)). However, the Ni finds a way around and diffuses in GeSn layer creating the NiGeSn phase.

In figure (14b) the cross section of the sample shows a clear indication of the formation of a thin layer of around 40nm of NiGeSn. The sample for which cross section is shown was annealed in the 450°C.

Figure (14) (a) Surface SEM images before and after Ni deposition and annealing for the compressive strained GeSn (b) cross sectional image of this sample after Ni deposition and annealing
Figure (15) *Tin dot with nickel remained on a side*

For the strain relaxed sample, a similar observation is noticed that some of the Sn remained unreacted on the surface after the annealing (see figure (16a)).

Figure (16)  a) Surface SEM images before and after Ni deposition and annealing for the strain relaxed GeSn with 70nm thickness  b) Cross section for the strain relaxed GeSn after Ni deposition and annealing
The cross-section image of this sample in figure (16b) indicates that a thicker NiGeSn layer is formed as compared with the compressive strained structure. The main reason may be that the strain-relaxed GeSn contains higher defect densities which act as easy paths for the Ni diffusion during germanide formation.

![Surface SEM images before and after Ni deposition and annealing](image1)

![Cross section for the tensile strained GeSn after Ni deposition and annealing](image2)

*Figure (17) Epitaxial layers for a tensile strained structure of GeSn, a) Surface SEM images before and after Ni deposition and annealing b) Cross section for the tensile strained GeSn after Ni deposition and annealing*

For tensile strained structure of GeSn, there are large Sn dots on the surface (see figure (17a)). These dots disappear after Ni deposition and annealing at 450°C. There are two possible interpretations for this observation. Either the Sn dots have made Sn oxide with oxygen and evaporated from the surface during the RTA or the Sn interacted with the Ni to create the NiGeSn phase. In both cases, more experimental work is needed to prove the theories. Figure (17b) shows that the NiGeSn layer thickness is 50-70 nm. The relatively thick layer of virtual GeSn layer in the tensile structure introduces high defects densities. These defects provide an extra path for the Ni atoms to diffuse into the GeSn layer and consequently lead to thicker NiGeSn formation; therefore we observe a thicker layer in the case of the tensile structure as compared to compressive structure.
4.2 Rocking Curves

Rocking curves (RC) are used to study the crystal quality in thin films and bulk crystals. The rocking curve is the x-ray (ω-2θ) measurement performed on wafers to identify the substrate and different layers deposited on the wafer.

Figure (18) The ω-2θ measurement for (GeSn / Ge /Si substrate)

Figure (18) shows a typical RC for GeSn/Ge/Si substrate structure. The silicon peak is located between 34- 35 degrees on the x-axis with the highest intensity. The Si substrate produces higher intensity than the other two deposited layers on the substrate because of its thickness. The substrate thickness is around 500µm compared to the 50nm thickness of the GeSn layer. The Ge virtual layer is located on the left of the Si substrate peak, around 33 degrees, the Ge lattice mismatch with Si lattice is less than the GeSn lattice mismatch therefore we notice the position of the GeSn peak even much further than Ge virtual peak.
Figure (19) RCs for compressive strained GeSn structure before and after the Ni deposition. Strain degradation appears for the GeSn layer after Ni-germanide formation.

Figure (19) is a RC for the compressive strained GeSn structure in which GeSn peak is visible in the blue graph at -5500 seconds (ω/2θ). The sample is measured before Ni deposition and RTA annealing. However after Ni deposition and RTA annealing at 450°C, the GeSn epitaxial layer disappeared totally. This is the indication of strain degradation due to Ni diffusion into the GeSn layer and formation of NiGeSn phase. Another possible conclusion is that the GeSn layer has been consumed by the NiGeSn formation.

Figure (20) RCs for strain relaxed GeSn structure before and after Ni deposition. GeSn layer is not affected.
For relax strained GeSn, according to the RC, the layer is not affected by the germanide formation. There is no strain relaxation because the structure itself is a relaxed GeSn structure; however we observe relatively low intensity for the GeSn strain relaxed structure as compared to the one before annealing (see figure (20)). This is expected because some of the GeSn in the layer was consumed by the formation of the NiGeSn phase.

The tensile strained (GeSn) structure has two (GeSn) layers with different Sn content on the Si substrate. In GeSn tensile structure the upper layer GeSn has lower Sn content as compared to the GeSn layer below it to create the tensile strain effect.

From the comparison between the compressive strained, tensile strained and strain relaxed structures (figure (21)) we notice the tensile has lowest intensity relative to both compressive (the highest) and relaxed in the middle. The RC for the NiGeSn after RTA annealing in 450°C for tensile structure has lower intensity as compared with the compressive and strain relaxed structures.
4.3 X-ray Reciprocal lattice mapping measurements

Figure (22) shows three different graphs for X-ray reciprocal lattice measurements. The measurements are for structures (compressive, tensile and relaxed GeSn) before and after annealing (RTA in 550°C in N₂ gas). The reciprocal lattice images were created by combining 220 RC measurements for each sample.
For the compressive strained structure, the GeSn peak is clearly sharp before NiGeSn formation, however after the formation of NiGeSn still there is a sharp peak of GeSn but moved upward towards the Ge peak as it is shown on the figure (22).

Furthermore, it shows clear indication of strain relaxation due to the formation of the NiGeSn phase. The strain relaxation is represented by the GeSn peak which is shifted in a perpendicular direction towards the Ge peak on Y-axis. The strain relaxation is caused by getting Sn atoms out of the GeSn lattice structures.

Regarding the tensile strained GeSn structure, the GeSn peak is not clearly seen because of the multilayer structure of tensile strained GeSn epitaxial layer, however it is expected to be on the top of the Ge peak, as it is expected for the tensile structure (See figure (22) (tensile)). After the NiGeSn formation process, the GeSn peak has shifted downward to the Ge peak direction. The downward shift of GeSn peak is an indication of strain relaxation caused by the formation of NiGeSn phase.

For the strain relaxed GeSn structure, the structure itself has no strain so there is no noticeable change in the strain direction, however there is some peak shrinking after the NiGeSn formation process, but it is not due to the strain relaxation but to the lattice thermal change, as the sample is heated to 550°C and then cooled down to room temperature. Consequently, the GeSn subjected to thermal annealing is led to thermal lattice change.

The conclusion for the reciprocal lattice measurements is that the shift of GeSn layer after Ni deposition and annealing to form NiGeSn phase for strained GeSn structures is always towards the Ge peak.
4.4 X-ray diffraction and phase identification

A phase is a crystalline solid with a regular 3-dimensional distribution of the atoms. The identification of multiple phases in NiGeSn sample is the main application of X-ray powder diffraction. The measured diffraction peak positions and intensities for NiGeSn are like a fingerprint of a particular crystalline phase. Identification is performed by comparison of the measured pattern of the NiGeSn with the ones in the reference database using a search-match. [19]

Empyrean multipurpose and Expert high resolution X-ray diffraction were applied to analyze the theta-2 theta measurements of the NiGeSn phases that were formed on three GeSn epitaxial layers (compressive, tensile and relaxed GeSn) with the same Sn content.

By comparing the three structures (figure (23)), the low resistivity phase of NiGeSn was identified in all three structures in the same relevant theta angle. The reflection of the X-ray from different angles appears for the entire three samples in the same position as an indication of the formation of NiGeSn phase. Different peak intensities represent different NiGeSn thicknesses. It is noticeable the β-Sn agglomeration is associated with the phase formation.

Figure (23) The x-ray θ-2θ measurements of NiGeSn phases are similar for all the three types of structures.
4.5 Four point resistivity measurement

Figure (24) represents the resistivity measurement for three different GeSn (compressive, tensile and relaxed strained) structures in three different RTA annealing temperatures (350, 450 and 550°C). For the compressive strained GeSn samples (see figure (24a)), a general pattern is observed for the resistivity change with temperature variation from 350°C to 550°C for all samples.

Furthermore, at 350°C of RTA, the temperature shows high resistivity values as an indication of the formation of the Ni rich phase N,GeSn.

At 450°C of RTA, the temperature shows low resistivity values as an indication of the formation of the mono Ni with GeSn or NiGeSn phase.

As the RTA temperature rises to 550°C again a higher value for resistivity is measured as an indication of the formation of GeSn rich phase, the same exact patterns occurs for the tensile and relaxed GeSn samples as it is shown in figures (24b,c).

The thermal stability of the formed NiGeSn phase is highly dependent on the Sn content. With higher Sn content it is expected to see lower thermal stability at 550°C. It is noticeable that the samples measured at 550°C have different resistivity values due to the different Sn content.

In figure (24a) each resistivity measurement is labeled with a particular name. The first curve from the strain relaxed resistivity measurements is labeled as (AGseedGSB1190T290). This label defines several layers and the temperature in process as AGseed is the seed layer of Ge which is deposited before the GeSn layer deposition, GSB is the GeSn with B doping, the 1190 is the Sn flow during the deposition and the T290 is the deposition temperature in CVD.

Furthermore, it is noticeable from the same resistivity data curve, the higher value for the resistivity at 550°C annealing temperature as compared to the other curves for the compressive structure measurements (see figure (24a)). The explanation is the difference of the Sn content in each sample measured, which leads to higher thermal stability in 550°C. In another argument it proves the dependence of the thermal stability on the Sn content.
Figure (24) Resistivity measurement for the three different GeSn structures in three different temperatures (350, 450 and 550°C)
Chapter five

5.0 Conclusions
The GeSn epitaxial structure influences on the formation of the NiGeSn phase. The compressive strained GeSn structure which forms NiGeSn phase in 450°C makes the thinnest germanide layer as compared with the other structures. The formation and thermal stability of NiGeSn is dependent on the Sn content. The segregated Sn atoms during epitaxy process form dots on the GeSn surface. These dots act as a barrier for Ni diffusion into the GeSn layer. At 450 °C of RTA of NiGeSn formation, is the annealing temperature to create the lowest resistivity value for that phase. The NiGeSn phase formation introduces point defects to the GeSn layer which lead to strain relaxation.

It is clear that GeSn and NiGeSn are promising materials for Ge based devices in thermoelectric application, for both application as germanide between the thermoelectric based nanowires and the metal contacts or as a material for nanowires itself.

5.1 Future work
There are ways to improve the novel property of the GeSn in terms of thermal stability and Sn segregation. It has been certain improvement work done by our group in KTH to get higher thermal stability of GeSn by introducing very low percentage of Carbon (C) to GeSn epitaxial layer. Reducing Sn segregation by introducing low percentage of Si to GeSn epitaxial layer is another possible improvement[20]. There is a great chance for NiGeSnSiC to become the new promising material for electronic, photonic and thermoelectric future applications.
References


