Precipitation of dopants and its long term effect on thermoelectric performance

Internship at RGS Development B.V.

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1. Abstract
In this internship the precipitation over time in SiGe alloys at several temperatures was investigated. The Lifshitz-Slyozov model was applied to find out long term degradation of thermoelectric performance. Precipitation rate and equilibrium concentration was fitted to the measured results. The fit for the p-type thermoelectric materials were good although the precipitation rate was higher than expected. The reason for this deviation will lie mostly in the difference in the experimental procedures compared to literature. Due to this there are more defects which greatly increase diffusion. For phosphorus more work is needed for obtaining a good fit of the parameters used here.

2. Introduction

Figure 1: the open circuit voltage and resistance of a thermoelectric module over time. At approximately 550 and 1000 hours the furnace was temporarily turned off.

At RGS\(^1\) development, full modules have been shown to have an increase in resistivity and Seebeck coefficient over time (see figure 1). Especially P-doped material shows an increase in resistance. The Seebeck coefficient levels off after a while. Precipitation of the dopants used in the thermoelectric devices is one of the causes of these phenomena. The goal of this study is to estimate the extend dopant precipitation is the cause of this effect compared to processes other than the internal material properties. This process will be studied on several compositions and dopant levels relevant to the application of the material. The materials investigated will be both the material used for thermoelectric generation legs and the bridging interconnection material (see figure 2). The aging tests will be done with annealing tests. The temperatures of the annealing were chosen either on the basis of application or modelling. The time of the internship is short compared to the lifetime which has to be achieved. Tests longer than the tests performed in this internship will need to be performed to check and improve the model. So the work presented here must be seen as the start of the work as more data is required to have better accuracy.

\( ^1\) Ribbon Growth on Substrates

2.1. Precipitation model
The basis for the models described in this study is from Slyozov and Lifshitz (Lifshitz & Slyozov, 1961). This model describes the precipitation rate of material in a matrix. This model has been used in literature to characterise performance degradation before for both boron and phosphorous in SiGe alloys (Burgess
& Nasby, 1974; Ekstrom & Dismukes, 1966; Savvides, 1983; Savvides & Rowe, 1981; Shukla & Rowe, 1981a, 1981b) but not for the composition and dopant level applicable for this study. In this study the carrier concentration over annealing time will be estimated for different temperatures.

This model is a model for the growth of a precipitate phase in the solid material. The precipitates formed are a B$_2$Si (see figure 5) which is a different phase form the original lattice or a (Si-Ge)P forming a pseudo lattice coinciding with the host matrix (Slack & Hussain, 1991). These phases are electronically inactive. These phases are grown because of the supersaturation of the dopants in the alloy matrix (for the phase diagrams see figure 2 and 5 (Olesinski & Abbaschian, 1984; Olesinski, Kanani, & Abbaschian, 1985)).

So the carrier concentration decreases over time as the dopants are added to this new precipitate phase. The model describes a process where there are nuclei having a certain size that is larger or smaller than a critical size. Above this size the particles will grow and smaller particles dissolve. This requires moving dopants through the solid. This only occurs at elevated temperatures as the diffusion is too slow at room temperature. The diffusion coefficient will be collected from literature. The equations used in this model are (Shukla & Rowe, 1981b):

- **Equation 1**
  \[ Z^3 = At + B \]

- **Equation 2**
  \[ Z = \left(\frac{c_0 - c_e}{c(t) - c_e}\right) \]

- **Equation 3**
  \[ A = A' \left(\frac{c_0 - c_e}{c_e}\right)^3 \]

- **Equation 4**
  \[ A' = 4D \frac{dRT}{9c_p} \left(\frac{R}{2M}\right)^2 \]

In these equations \( Z \) is the inverse unprecipitated fraction of excess solute (Savvides, 1983), \( B \) is an integration constant close to one (Shukla & Rowe, 1981b), \( A \) is an integration constant (s$^{-1}$), \( c_0 \) is the initial carrier concentration (cm$^{-3}$), \( c_e \) is the equilibrium carrier concentration (cm$^{-3}$), \( c(t) \) is the carrier concentration (cm$^{-3}$), \( D \) is the diffusion coefficient (cm$^2$/s), \( c_p \) is the concentration of the dopant in the precipitate particles (cm$^{-3}$), \( d \) is the density (g/cm$^3$), \( R \) is the gas constant (8.314 J/K*mol), \( T \) is the temperature (K), \( M \) is the mean atomic weight (g/mol) and \( \sigma \) is the interfacial surface tension (J/m$^2$). Reworking these formulas for the \( c(t)\):

- **Equation 5**
  \[ c(t) = \frac{c_0 - c_e}{\left(\frac{c_0 - c_p}{c_e}\right)^3} \left(\frac{dRT}{9c_p} \left(\frac{dRT}{2M}\right)^2 \theta + B\right)^{1/3} + c_e \]
With this model it was attempted to fit the data on $c_e$, D and a time independent $A'$ (=A/DT). If successful an exponential can be fitted to the equilibrium concentration and an Arrhenius plot to the diffusivity. The values of D and $c_e$ should then be compared to literature values. The fit of D, $c_e$ and $A'$ was obtained through a least squares method on the difference between the modelled carrier concentration and the carrier concentration calculated from the measurements.

The initial values of the fitting were obtained from literature of similar materials. For the boron equilibrium concentration the phase diagram will be used (Olesinski & Abbaschian, 1984). For phosphorus equilibrium concentration data can be found in literature for several different compositions of the SiGe alloys (Burgess & Nasby, 1974). With increasing germanium content the solubility decreases (Burgess & Nasby, 1974; Christensen, 2004). This means that the equilibrium concentration for phosphorus found in this study should be higher than the equilibrium found for Si$_{81}$Ge$_{19}$ found in (Burgess & Nasby, 1974).

Diffusivity data can be found in (Christensen, 2004). Phosphorus has a higher diffusivity in Ge than boron leading to higher precipitation rates (Shukla & Rowe, 1981b). The diffusivity of the dopants in silicon is similar (Shukla & Rowe, 1981b). Typically $A^*$ is found to be around 2000 times higher for phosphorus than for boron in SiGe alloys (Shukla & Rowe, 1981b). This means that initially the increase in resistivity of a module is likely due to phosphorus precipitation.

Figure 5: Phase diagram of phosphorus in silicon (Olesinski & Abbaschian, 1984).

For boron this model can be poor at explaining the initial concentration profile as the
nucleation is not included (Savvides, 1983). In an addition to this model the concentration has an initial parabolic growth rate (see figure 6) instead of a solely linear behaviour (Savvides, 1983). This was explained by a soliton model (Savvides, 1983). The initial stage for this would yield the equation (Savvides, 1983):

\[ Z^3 = Ct^{3/2} \]

However in this internship the initial long term equation 5 will be used because it has been able to predict long term behaviour in several studies (Dismukes, Ekstrom, Steigmeier, Kudman, & Beers, 1964; Shukla & Rowe, 1981b).

2.2. Conversion of Seebeck coefficient to carrier concentration

The model will be used to calculate the performance of the material over long term annealing tests based on the short annealing tests done during the internship. The carrier concentration, Seebeck coefficient and resistivity are related to the Fermi energy. The Seebeck coefficient in a single band model is given by (Slack & Hussain, 1991):

\[ S = \pm \frac{k}{e} \left( \frac{(2 + s)F_{1+s}(\delta^*)}{(1 + s)F_s(\delta^*)} - \delta^* \right) \]

The +/- sign is for the valence or conduction bands respectively (Slack & Hussain, 1991). \( K \) is the Boltzmann constant, \( e \) is the charge of the electron, \( F_{1+s} \) and \( F_s \) are the fermi integrals and \( \delta^* \) is the reduced fermi level (= \( \delta/kT \)). \( s \) is the scattering parameter. Where \( s=0 \) means a scattering from lattice vibrations and \( s=2 \) charged impurity scattering (Slack & Hussain, 1991). \( S=1 \) is a mixed scattering and most applicable here due to the carrier concentration used here (see figure 7) (Slack & Hussain, 1991). The effective mass is not dependent on germanium content (Slack & Hussain, 1991).

Figure 6: \( Z^3 \) over time at 1100 K in the soliton model (Savvides, 1983). 1 and 2 were produced with zone levelling and 3 was produced with hot pressing (Savvides, 1983).

Figure 7: Seebeck coefficient versus carrier concentration for SiGe samples at different germanium content at 300K.

The carrier concentration can also be calculated from the fermi integrals with equation 8.

\[ \frac{[n]}{[p]} = \frac{4\pi \left( 2m^*kT \right)^{3/2}}{\hbar^3} F_{1/2}(\delta^*) \]
In this equation \([n]/[p]\) means the carrier concentration, \(m^*\) is the effective mass in units of electron mass and \(h\) is the Planck’s constant.

### 3. Experimental

The samples are prepared by the ribbon growth on substrates (RGS) technique (Nakajima & Usami, n.d.) (see figure 8). In this process a casting frame containing the liquid reactants is placed above a transport line with substrates. On the cooled substrate the alloy crystallizes rapidly and is transported to a cooldown section of the process. This technique has higher dislocation density and less homogeneity (Nakajima & Usami, n.d.) than the typical fabrication methods used in literature like zone levelling and hot pressing (Savvides, 1983). In the wafers of the RGS process there are many concentration gradients and interfacial boundaries.

![Figure 8: the principle of the RGS wafer production process (Nakajima & Usami, n.d.)](image)

The samples would then be cut (\(\sim 40.20*13.00\) mm) and grinded. On the samples four point probe resistivity on both sides of the sample and Seebeck measurements were performed. The higher doping level samples are tested as possible interconnection material that connects the thermoelectric generating legs. After measuring the as grown sample the samples were annealed at 927°C, 750°C or 600°C for 100 and 300 hours for boron doped samples and 750°C, 600°C and 400°C for 10 and 100 hours for phosphorus doped samples (see table 1). 600°C and 750°C are possible application temperatures and 927°C and 400°C were chosen as useful for the model. 927°C is the temperature at which sufficient boron precipitation should be occurring as to have measurable change in Seebeck coefficient. At short annealing times there should be a maximum in phosphorus precipitation rate observable between 500°C and 600°C (Burgess & Nasby, 1974). So together with 750°C, 400°C would give a point on each side of the maximum.

At each of these stages the resistivity and the Seebeck coefficient are measured. The annealing is done in air which causes oxidation of the surface. Etching is done with a 5% aqueous HF solution to remove the SiO\(_2\) layer that formed on the surface.

Accurate data on the phosphorus concentration in the n-doped SiGe will be provided by Elkem with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

Hall measurements will be performed by CrisMat\(^2\) to accurately measure the active carrier concentration and hall mobility. As of writing the results of the Hall measurements were not yet received.

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4. Results and discussion

4.1. ICP data

In table 1 it can be seen that the actual phosphorus content is different from the phosphorus content calculated from the mass balance. Also from the same feedstock there is a varying amount of phosphorus in the samples. The varying initial concentration seen in figures 21-23 could be attributed to this.

4.2. Seebeck and resistivity measurements

In the following sections the measurements will be discussed. P-type doping will be discussed first after which n-type will be presented. In figure 9-14 are shown the results of the resistivity and Seebeck measurements.
after time annealed on different temperatures for boron doped samples. The measurement results for phosphorus doped samples are shown in figure 21-23. Also in these figures the calculated carrier concentration and power factor are included. The carrier concentration graphs also contain the modelled values.

4.2.1. Boron

Figure 9: Results of the Seebeck and resistivity measurements, the carrier concentration and the power factor for Si$_{85-x}$Ge$_{15}$B$_x$ x=0.25 at 927°C (green), 750°C (red) and 600°C (blue). Modelled carrier concentration is displayed with the coloured lines. The black lines are for tracking individual samples.

There is a spread in the Seebeck measurement results for the 0.25at% B samples that disappears after the annealing step (figure 9 & 10). The Seebeck coefficient is slightly higher for the 10 Ge at.% than the 15 at.% Ge. This is consequently also seen in the carrier concentration and could therefore mean that the equilibrium concentration is nearly reached. The calculated equilibrium concentration is therefore close to the initial concentration.

The initial concentration calculated from Seebeck is 5.31*10$^{19}$ cm$^{-3}$ for the Si$_{84.75}$Ge$_{15}$B$_{0.25}$ and 5.58*10$^{19}$ cm$^{-3}$ for Si$_{89.75}$Ge$_{10}$B$_{0.25}$. This is approximately 0.11 at%, which is less than half of the intended boron content. The carrier concentration calculated here is an estimate of the active carrier concentration. A lower active carrier concentration than boron content suggests that precipitation has already occurred to a significant extent or the effective mass is off. The Hall measurement results should yield an accurate effective mass which will make the conversion of the Seebeck coefficient to carrier concentration more accurate. Because m* = 1 is used the carrier concentration could be incorrect.

In this internship it was decided not to do an annealing step for dissolution prior to the measurements. This could therefore have caused the variation in the initial carrier concentration and the lower active concentration.

This proximity to the equilibrium carrier concentration is also seen in the resistivity results (figure 8 & 9). The resistivity changes little over time in these samples.

The power factor seems to stay relatively stable on average after the initial annealing step.
Figure 10: Results of the Seebeck and resistivity measurements, the carrier concentration and the power factor for Si$_{90-x}$Ge$_{10}$B$_x$, $x=0.25$ at 927°C (green), 750°C (red) and 600°C (blue). Modelled carrier concentration is displayed with the coloured lines. The black lines are for tracking the individual samples.

When the dopant level is increased the different precipitation rates for the different temperatures become more apparent (see figure 9-14). This can be seen in both the Seebeck coefficient and the resistivity measurements. The variation in the initial Seebeck coefficient and carrier concentration is much lower than in the low dopant level samples. Also here the calculated concentration is lower than the intended dopant level (0.17 vs 0.35 at.% respectively).

Over time the power factor seems to increase. In the Si$_{84.65}$Ge$_{15}$B$_{0.35}$ material (figure 10) the initial concentration is $8.3 \times 10^{19}$ cm$^{-3}$ and has therefore, similar to the samples presented before, a lower initial concentration than intended dopant level (0.17 versus 0.35 respectively).

With increased dopant level the Seebeck coefficient, as expected, has increased (see figure 10).

The driving force of the precipitation has increased as the difference between the initial concentration and the equilibrium concentration is larger these samples. With increased temperature it can be seen that the precipitation rate increases as well due to a faster diffusion.
Figure 11: Results of the Seebeck and resistivity measurements, the carrier concentration and the power factor for 0.35% B and 15% germanium in the SiGe alloy at 927°C (green), 750°C (red) and 600°C (blue). Modelled carrier concentration is displayed with the coloured lines. The black lines are for tracking individual samples.

### 4.2.1.1. Interconnection material

In the following section the interconnection materials are discussed. These have a higher doping level than the thermoelectric material as the conductivity of material is more important. 0.5, 2, and 3% are used but also here it can be seen is lower (0.21, 0.39 and 0.46 at.% respectively), meaning a significant portion of boron has already precipitated or the conversion from Seebeck coefficient to carrier concentration is wrong.

With the higher dopant level the effect of temperature on the precipitation rate becomes more significant. At this timescale the carrier concentration of these p-type thermoelectric materials does not change much at 600°C. This will make it difficult to have an accurate prediction of the precipitation rate over larger timescales. The diffusivities and equilibrium concentrations at higher temperatures can be used.
Figure 13: Results of the Seebeck and resistivity measurements, the carrier concentration and the power factor for Si$_{90-x}$Ge$_{10}$B$_x$, $x=2$ at 927°C (green), 750°C (red) and 600°C (blue). Modelled carrier concentration is displayed with the coloured lines. The black lines are for tracking individual samples.

In figure 13 and 14 the 2 and 3% boron doped sample measurements are displayed. In these figures it can be seen that there is a large increase in absolute Seebeck coefficient and resistivity already in the first annealing step.

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The Seebeck coefficient measured in the samples heated at 927°C is higher than the S measured in the low dopant level samples. This is quite surprising as that would suggest that the carrier concentration drops below the carrier concentration of the lesser doped samples. The model fitted on these data points suggests that the precipitation reaches the asymptotic region of the model within the first hours of annealing. Therefore these measurements give a good idea of the
4.2.1.2. Modelling results

In figure 15-17 the carrier concentration is modelled for five years (43800 hours). Here it can be clearly seen that increasing temperature increases the precipitation rate. In the case of 927°C at 2 and 3% the material has nearly reached equilibrium within the first hour in the current model. This precipitation rate is much higher than found in literature (Savvides, 1983; Shukla & Rowe, 1981b), although the Ge content of the alloy is different in these instances. To accurately indicate the actual rate, measurements in the first hour or two would be helpful.

Table 2: Fitted equilibrium concentrations for the two alloy compositions.

<table>
<thead>
<tr>
<th></th>
<th>600°C</th>
<th>750°C</th>
<th>927°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si_{85,5}Ge_{15}B_{x}</td>
<td>1.9E+19</td>
<td>2.0E+19</td>
<td>2.1E+19</td>
</tr>
<tr>
<td>Si_{90,5}Ge_{10}B_{3,8}</td>
<td>3.8E+19</td>
<td>4.0E+19</td>
<td>4.3E+19</td>
</tr>
</tbody>
</table>

In table 2 the calculated equilibrium concentration can be found. Over time the modelled carrier concentrations will tend to these values. The rate differs for each temperature and alloy composition. The diffusion for Si_{90,5}Ge_{10}B_{3,8} should be higher than for Si_{85,5}Ge_{15}B_{x} (Christensen, 2004). For both boron and phosphorus D and A’ are more difficult as these values are both contained in the overall rate A, because of this it is difficult to be sure of the individual components.

Figure 15: Carrier concentration plotted for five years at 600°C for the different boron dopant levels and germanium content in the SiGe alloy.

According to the model presented here the precipitation in Si_{90}Ge_{10} is faster (see figure 14 & 15, red & blue lines). This is then indeed caused by the increase in diffusivity. With a higher concentration of dopants the distance between the dopants decreases. This means that the distance to a growing precipitate particle decreases. The precipitation rate would then be higher. This could possibly explain why the 3% boron doped samples decrease below the 2% doped samples. This might, however, also be due to an inaccurate model as for 600°C the measurements were only done in the flat part of the carrier concentration profile.

Figure 16: Carrier concentration plotted for five years at 750°C for the different boron dopant levels and germanium content in the SiGe alloy.
In figures 17-19 the $Z^3$ over time at 600, 750 and 927°C is presented. The values displayed are calculated using equation 2. With the current model $Z^3$ should depend linearly on time (see equation 1) (Shukla & Rowe, 1981b). It can be seen that for many of the samples this is not the case. At present the plots also don’t display the initial parabolic phase seen in the model which does incorporate the nucleation stage (figure 5) (Savvides, 1983). The annealing tests are too short to properly assess whether nucleation should be included in the model to improve accuracy.

**4.2.1.3. $Z^3$ behaviour**

Due to the larger diffusion in Si$_{90}$Ge$_{10}$ the change in $Z^3$ over time is larger as precipitates grow faster. Compared to figure 1 the change of $Z^3$ of Si$_{85}$Ge$_{15}$ is more similar as the value stays close to one for the data presented here. Si$_{90}$Ge$_{10}$ however increases much more rapidly in these cases.

The $Z^3$ for the highly doped samples in 927°C (figure 20) shows that these samples reach equilibrium rather quickly. These values of $Z^3$ are unprecedented in the attempts to model the behaviour of precipitation with this model (Savvides, 1983; Shukla & Rowe, 1981b).

**4.2.2. Phosphorus**

In figures 20-22 the measurements on the n-type materials are displayed. For Si$_{84.745}$Ge$_{15}$P$_{0.255}$ and Si$_{84.73}$Ge$_{10}$P$_{0.27}$ there is again a large spread in the Seebeck coefficient and resistivity measurements for the as grown materials. For 750°C the Seebeck coefficient is stable after 10 hours while at lower temperatures $S$ still decreases between 10 and
100 hours. The carrier concentration is also lower than the ICP data in table 1 just as was the case for boron.

The carrier concentration has less distinct behaviour at different temperatures than with boron. At 927°C and high boron concentration near equilibrium conditions were reached rather quickly, at 750°C the precipitation could be observed better while at 600°C the carrier concentration did not change much yet. For phosphorus this is less so. This probably makes the fit less accurate. Also for the phosphorus measurements it was more often found that the Seebeck coefficient increased in some annealing steps. This would mean that the carrier concentration would increase and therefore seems erroneous.

Figure 21: Results of the Seebeck and resistivity measurements, the carrier concentration and the power factor for Si$_{85}$Ge$_{15}$P$_x$, $x=0.255$ at 750°C (red), 600°C (blue) and 400°C (green). Modelled carrier concentration is displayed with the coloured lines. The black lines are for tracking individual samples. (Elkem feedstock)

In contrast to the measurements presented previously the power factor of the samples prepared with the Elkem feedstock for the SiP seem to have an overall increase in power.
factor (figure 20 & 21). This increase is not seen however in the RGS feedstock (figure 22).

Modelling results

Figure 24: Carrier concentration plotted for three years at 600°C for the different n-type dopant levels and germanium content in the SiGe alloy.

When the model fitted on the data in figure 20-22 is extrapolated for three years the result is figure 23-25. As discussed in the previous section however, the fit of the data is not ideal yet. But presently the model gives an equilibrium concentration between $3.3 \times 10^{19}$ and $5.3 \times 10^{19}$ cm$^{-3}$ depending on the temperature and composition. With the present fit the equilibrium concentration at 600°C for Si$_{90}$Ge$_{10}$P$_{0.27}$ is lower than for 400°C. This is caused by an erroneous fit, inaccurate measurements or differences in the samples used for each of the measurements. A similar problem has arisen for Si$_{85-x}$Ge$_{15}$P$_{x}$ where $x=0.45$ to $0.6$. The equilibrium concentration therefore would appear to be higher in the case of the materials produced from the feedstock of RGS.

Figure 25: Carrier concentration plotted for three years at 400°C for the different n-type dopant levels and germanium content in the SiGe alloy.
4.3. Deviations from the model

The samples in this study are fabricated differently than what is found in literature (Shukla & Rowe, 1981b). As discussed in the experimental section the rapid crystallization of the wafers causes a higher amount of dislocations and Ge content gradients (Nakajima & Usami, n.d.). The material used in this study is not as crystalline and not as homogenous. Ge content has influence on the diffusion of dopant, at these compositions an increase in germanium content increases diffusivity of phosphorus, while decreasing it for boron (Christensen, 2004). Due to this inhomogeneity and increased diffusivity in germanium rich alloys, the overall diffusivity will likely increase for phosphorus. The opposite can be true for boron that overall diffusivity increases due to increased diffusivity in germanium poor regions. Also the different regions cause defects and an increase in defects leads to higher diffusivity as the activation energy is lower. According to (Zamanipour, Krasinski, & Vashaee, 2013) it should take over 30 minutes to reach equilibrium conditions. In this study they used Si$_{78.4}$Ge$_{20}$B$_{1.6}$ and during cycle tests for thermoelectric performance they grew whiskers of boron precipitate (see figure 27). The precipitates are located at the crystallite boundaries as boron atoms are trapped there (Zamanipour et al., 2013). The timescale in that study (>30 min.) is much more similar to what we measured than in the models for precipitation in literature discussed in this report (Savvides, 1983; Shukla & Rowe, 1981b).

4.3.1. Oxidation effects

Oxidation will also play a (smaller) role in the increase of diffusivity of the material. The thermoelectric panels will be used in air so it makes the most sense for this study to do the
annealing tests in air instead of in vacuum or argon environment. This does mean however that oxidation will take place. The oxidation of the surface of the samples will increase the diffusion of the dopants near to the surface (Christensen, 2004). The depth of this increased diffusion is typically around a few hundred nm depending on time and temperature of oxidation (Packan & Plummer, 1990). Since the thickness of the samples ranges from ~0.5mm to ~1.2mm this will have a varying effect on the different samples. The mechanism of this is an increase in diffusion via interstitials (Christensen, 2004). When the oxide layer grows there is an increase in strain on the lattice (Christensen, 2004). This causes self-interstitials which enhance the diffusion of the dopants (Christensen, 2004). The oxidation can be catalysed by Ge which would make the impact on Si$_{88}$Ge$_{12}$ larger (LeGoues, Rosenberg, Nguyen, Himpsel, & Meyerson, 1989).

5. Further work
When a model is made and data is fitted, it is always better to increase the number of data points to increase accuracy. This will be especially crucial for understanding the behaviour of the phosphorus precipitation. The amount of measurements might be too limited. For an accurate prediction of long term behaviour equilibrium concentration and precipitation rates need to be well established. For this the annealing tests have to be sufficiently long, while for Si$_{88}$Ge$_{12}$B$_2$ and Si$_{87}$Ge$_{10}$B$_3$ it might be helpful to have measurements within the first hours. To estimate whether the model for boron requires a nucleation stage longer tests are required. In this study the possibility of different phases than expected has been discussed. This might be shown with SEM measurements as done in (Zamanipour et al., 2013). As of the time of writing the results of the Hall measurements have not arrived. Hall measurements on different germanium content samples are required to have a more accurate active concentration and mobility assessment. With accurate data on the effective mass, equation 8 will yield better results, improving the validity of the fit of the model.

6. Conclusion
The goal of this study was to find out how the properties of the material change over time annealed. Annealing tests, Seebeck measurements and resistivity measurements were performed and the Lifshitz-Slyozov precipitate growth model was fitted to the data. Good fits were obtained for boron doped samples albeit with faster precipitation rate than expected. Especially at high boron concentration the precipitation is faster than expected. The increase in precipitation is due to the inhomogeneous material with a high dislocation density compare to literature where polycrystalline samples are used. For phosphorus the fit was worse most likely due to a lower amount of measurements.

7. Bibliography


