Fabrication and Thermoelectrical Power Factor of n-type Si85Ge15 Alloys

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Abstract. N-type Si85Ge15 alloys heavily doped with different dopant over a wide range of dopant have been fabricated by hot isostatic pressing. Influences of the carrier concentration and mobility of heavily doped n-type Si85Ge15 alloys on the thermoelectrical power factor are investigated. The experimental results indicate that thermoelectrical power factors of 31-38μWcm−1K−2 could be consistently achieved with carrier concentrations of 2.0-3.0 × 10^{20} cm−3 and carrier mobilities of 35-42 cm² V⁻¹ s⁻¹, However, many samples with suitable carrier concentrations do not always have high mobilities and high power factors. Some possible explanations for this behaviour are presented.

1. Introduction

Thermoelectric materials are a kind of semiconductor functional materials, which can be used to convert directly thermal energy to electricity or reversely in an environmental friendly manner. They are of great interest for applications in power generators and cooling devices. The performance of thermoelectric materials is qualified by the dimensionless figure of merit (ZT), which is defined as \((\alpha^2\sigma/\kappa T)\), where \(\alpha\), \(\sigma\), \(\kappa\), and \(T\) are Seebeck coefficient, electrical conductivity, thermal conductivity and the average operating temperature respectively. The Seebeck coefficient and electrical conductivity depend strongly on the Fermi level [1], which in return depends upon the carrier concentration, carrier mobility and temperature. Since the thermal conductivity depends only weakly on the carrier concentration \(n\)[2], the general effect of increase of carrier concentration would manifest itself in the figure of merit via the thermoelectrical power factor \((\alpha^2\sigma)\). Silicon-germanium (SiGe) alloys are established thermoelectric materials for high-temperature applications and have been used in space applications over a decade. The n-type SiGe alloys used in these devices were doped with phosphorus and the figure of merit was limited to 0.68×10^{-1–}0.74×10^{-1}K\(^{-1}\) over the range 600–1000°C. Higher values of figure of merit could not be achieved due to low carrier concentrations as a result of the limited P solubility in SiGe[3]. The presence of Ga was shown to increase the P solubility in SiGe alloys as a result of Ga-P ion pairing. The result leads to larger carrier concentration and permitting optimization of the electrical properties of SiGe alloys. By varying the contents of Ga and P, the carrier concentrations greater than 4 × 10^{20} cm^{-3} could be achieved, almost doubling the carrier concentration of standard SiGe alloys. This result clearly demonstrates the beneficial role of Ga in these systems. However, some of these samples with high carrier concentrations show low Seebeck coefficients due to overdoping[4]. A lot of works have focused on developing a better understanding of the requirements for consistently achieving a high power factor. In particular, the impact of both carrier concentration and mobility on power factor was investigated. In this study, samples were fabricated over a wide range of dopant concentrations to achieve carrier concentrations, within and above the optimum range. The effect of carrier concentration and mobility on power factor are
discussed. The second method for achieving high figure of merit is reduction of the thermal conductivity. The studies on reducing the thermal conductivity of p-type SiGe alloys by addition of inert scattering centres\cite{5-9} have shown that significant decreases can be obtained. In this study the first result on applying this technology to n-type SiGe alloys is presented.

2. Sample Fabrication and Test Equipment

Samples were fabricated by combining high purity of powders of Si, Ge, P and GaP and then hot isostatic pressed (HIP). Several of the resulting compacts were 18mm in diameter to allow evaluation of several samples with the same composition. Thin slices of φ10 × 1mm were cut from the ends of these samples for measuring Hall effect (Toyotechnica, Model RESITEST 8300). The samples were annealed at various temperatures to grow grains and heal the grain boundaries. Annealing temperatures were varied in the range 1200–1250°C. Annealing times for the samples were 5–10 h. Regardless of the anneal temperatures, the samples were quenched in air from 1100°C to ensure the maximal solubility of the dopants in the sample. Electrical conductivity and Seebeck coefficient were measured simultaneously to eliminate the abnormal behaviour resulting from dopant precipitation.

Electrical behaviour was measured from room temperature to 1000°C. The carrier concentrations and mobilities were measured by Hall measurement at 298K within an accuracy of 5% under an applied magnetic field of 0.39 T. The electrical conductivity of the samples was measured by four-probe techniques within an accuracy of 5%. To measure the Seebeck coefficient, heat was applied to the samples which were placed between two Pt-Rh discs. The thermoelectric electromotive force $E$ was measured upon applying small temperature differences ($\Delta T < 5$ K) between both the ends of the samples.

3. Analysis of test results

The Seebeck coefficients of the samples were determined from $E/\Delta T$.

![Figure 1. Room-temperature Hall mobility vs carrier concentration for hot isostatic pressed n-type Si85Ge15 with different dopants.](image-url)
SiGe alloys samples were fabricated with different Ga/P ratios from 1:1 to 1:7 with total P concentration varying between 2 mol% and 3 mol% and the total Ga content concentration ranging from 0.5 mol% to 1.8 mol%. The room-temperature Hall mobility vs carrier concentration for these samples is plotted in Figure 1. For comparison, the values obtained for P-doped SiGe alloys are also shown in Figure 1. The maximal carrier concentration observed for SiGe/GaP+P of $4.0 \times 10^{20} \text{ cm}^{-3}$ was obtained for a sample doped with 1 mol% GaP and 2 mol% P. The large increase in carrier concentration as a result of Group III–V interactions$^2$ is clearly shown in Figure 1. Additionally, it seems clearly that the mobility decrease is only due to the increase in carrier concentration. Comparison with P-doped SiGe alloys tends to confirming of this finding. The reason for the lower mobility with higher carrier concentration is that when the carrier concentration reaches a certain high value, there will be a number of carriers transfer to the energy band with higher energy levels, which lead to low mobility because the inter-valley carrier scattering. In addition, the carrier mobility goes down due to scattering by more impurities that were introduced into the SiGe alloys.

To identify the optimum electrical properties or the power factor ($\alpha^2\sigma$), changes of the power factor with carrier concentration and carrier mobility were investigated. All available power factor data on SiGe samples are plotted vs. room temperature carrier concentration in Figure 2. The power factor values are integrated average over the temperature 600–1000℃ range. The results indicate the estimated maximum power factor as a function of the carrier concentration.

![Power factor dependence of carrier concentration and carrier mobility.](image)

It is quite clear from Figure 2 that the P-only doped samples are underdoped while many of the GaP+P doped samples are overdoped. Although the rise in power factor as carrier concentration increases from 2.1 to $2.9 \times 10^{20} \text{ cm}^{-3}$ seems steep, it is indeed consistent with the transport theoretical properties model proposed by Vining$^{10,11}$. The experimental results indicate that the optimum carrier concentration needed to obtain these high power factor ranges from 2.1 to $2.9 \times 10^{20} \text{ cm}^{-3}$ and could
be achieved by doping of GaP or GaP+P. Although several samples in the optimum carrier concentration range have high power factors, the others have values below the maximum. Although some samples in the suitable carrier concentration range (2.1 × 10^{20} – 2.9 × 10^{20} cm^{-3}) indeed have high power factors, others have low power factor values. Several samples have similar carrier concentrations with different power factors, indicating that it is variations in the mobility that control the power factor. In order to further understand these behaviours, some of the present results are shown in Table 1 for the samples with high and low power factors, and in fact, the mobility does vary substantially in the samples with similar carrier concentrations.

Table 1. Power factor dependence of carrier concentration and carrier mobility.

| Carrier concentration (×10^{20}/cm^3) | Mobility (cm^2/ν·s) | Power factor (μW/cm·K^2) |
|----------------------------------------|----------------------|---------------------------|
| 2.15                                   | 41.60                | 24.18                     |
| 2.66                                   | 42.54                | 40.00                     |
| 2.72                                   | 36.45                | 25.82                     |
| 2.78                                   | 35.05                | 31.58                     |
| 2.83                                   | 37.43                | 34.02                     |
| 2.83                                   | 37.47                | 31.49                     |
| 2.82                                   | 40.72                | 28.47                     |
| 2.85                                   | 43.14                | 37.88                     |
| 2.91                                   | 36.79                | 28.18                     |
| 2.93                                   | 36.36                | 33.18                     |
| 2.95                                   | 37.18                | 28.19                     |
| 3.03                                   | 37.49                | 30.96                     |
| 3.14                                   | 38.38                | 35.35                     |
| 3.26                                   | 38.46                | 33.74                     |
| 3.15                                   | 36.90                | 37.33                     |
| 3.21                                   | 33.68                | 26.34                     |
| 3.42                                   | 30.64                | 27.08                     |
| 3.49                                   | 37.60                | 36.72                     |
| 3.60                                   | 32.91                | 30.38                     |
| 3.86                                   | 35.06                | 36.74                     |
| 4.00                                   | 27.98                | 20.82                     |

Figure 3. Morphology of samples doped with GaP before heat treatment.
4. Conclusions

The mobility varies for similar carrier concentration can be attributed to several reasons. The grain sizes for all the samples are similar, in the range of 40–80 μm. However, the dopant is probably not uniformly distributed in the samples since these samples were annealed with different temperatures and times. The morphology of these samples changed greatly before and after high temperature heat treatment. Figures 4 and 5 show the morphology of the samples doping with GaP before and after annealed at high temperature. It can be seen from Figure 4 and Figure 5 that before high temperature annealing, the morphology of the samples doped with GaP was quite homogeneous. However, after high-temperature annealing, the samples present inhomogeneous morphology and more porosities. The inhomogeneous alloy composition was shown to be advantageous in increasing the carrier concentration by providing reservoirs of dopant-rich areas. The experimental results show that the matrix regions correspond to higher Si concentrations and grain boundary regions correspond to higher Ge concentrations after high-temperature heat treatment. As experimentally observed, the dopant concentration in the Ge-rich area is higher. The alloys with inhomogeneous morphology may change the mobility of carriers. On the other hand, can be seen that after different high temperature annealing, the porosity increases as a result of out diffusion of the dopants in these samples. As the porosity increases, the mobility of carrier decreases. Based on the present results, a deeper understanding of the role of alloy homogeneity should be developed to persistently obtain high power factors. In summary, useful guidelines derived from this work include the determination of a narrow range of dopant concentrations which result in suitable carrier concentration and mobility. The key role of mobility in achieving high power factor has been demonstrated. Although not all the factors affecting the mobility have been identified, substantially gains in further understanding the process have been made and high power factor can be achieved.
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