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Seebeck Coefficient of Czochralski SiGe Alloy at High Temperatures*

Suo Kainan[1,†], Zhang Weilian[1], Niu Xinhuan[2], and Jiang Zhongwei[1]

(1 *Semiconductor Material Institute, Hebei University of Technology, Tianjin* 300130, *China*)
(2 *Institute of Microelectronics, Hebei University of Technology, Tianjin* 300130, *China*)

Abstract: To investigate the possibility of improvement in the thermoelectric properties of SiGe alloys, we examined several different silicon-germanium alloys with different contents, orientations, and electric conductive types. The thermoelectric properties of single crystal SiGe alloy were compared with those of poly-crystals. Experiment results show that the Seebeck coefficient of the sample depends on the temperature. All the samples show a maximal Seebeck coefficient in the temperature range of 700～900K. The Seebeck coefficient of the sample with ⟨111⟩ orientation is smaller than that of the sample with ⟨100⟩ orientation at the same temperature. The Seebeck coefficient of the SiGe alloy also depends on Ge content.

Key words: SiGe alloy; Seebeck coefficient; thermoelectric; crystal
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1 Introduction

Silicon-germanium (SiGe) or germanium-silicon (GeSi) alloy is a complete solid solution semiconductor with a cubic diamond-type structure. SiGe forms a complete range of solid solutions. According to composition, the lattice parameters of the solid solution follows Vegard's law closely from 0.566nm (pure Ge) to 0.543nm (pure Si), while the band gap changes from 0.66eV (Ge) to 1.12eV (Si). For any of the compositions, the solidus temperature lies between the melting points of the elements of 1693 and 1231K. Thus SiGe alloys are important for both microelectronic and optoelectronic devices and various function materials in view of the potential for band gap and lattice parameter engineering they offer. Bulk SiGe crystals also have applications in photo-detectors, X-rays, neutron monochromators, etc.

The best known application of SiGe alloys is as a material for thermoelectric power generators at elevated temperature[1]. In fact, SiGe thermoelectric devices have been successfully used as a power generator with radioisotope in deep space probes such as Voyager and Galileo. Now, SiGe has attracted increasing interest as a material with environmental compatibility.

The maximum possible conversion efficiency of SiGe alloys has been discussed theoretically by Abeles[2] and Yonenaga *et al*.[3,4]. A typical thermoelectric alloy with $Si_{0.7}Ge_{0.3}$ composition and a solidus temperature of 1300K has been suggested theoretically[5]. Slack and Hussain[6] have suggested that a high quality single crystal of SiGe alloy might be the most useful material without a boundary scattering effect. For such a theoretical expectation, it is necessary to use bulk single crystals of SiGe alloys with high purity and quality. Additionally, a single crystal has many advantages, such as mechanical stability and uniformity.

The obstacle to conducting such a project has been the difficulty in growing bulk single crystals of SiGe alloys of a suitable size due to a wide separation of the solidus and liquidus and the differences in the densities, lattice parameters, and melting temperatures of the constituent elements. Recently, one of the present authors has succeeded in growing bulk crystals of SiGe alloys by the Czochralski technique[7,8].

Jiang[9] investigated the Seebeck coefficient of p-type CZ-SiGe (Ge 5wt%) single crystals with

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† Corresponding author. Email: suokainan211@sohu.com
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〈111〉 and 〈100〉 orientations at lower temperatures, and he found that there was an obvious difference between them. But he has not investigated this at a higher temperature and other compositions.

2 Experiment

2.1 Sample preparation

SiGe bulk crystals with different Ge concentrations were grown by the CZ technique in a high-purity flowing argon gas atmosphere (665Pa). The very low pulling rates during the crystal growth from head to tail were in the range of 0.8～0.1mm/min. The silicon seed was rotated clockwise at a constant rate of 15r/min, and the crucible was rotated counterclockwise at a constant rate between 3 and 5r/min. The crystal diameter is 60mm, and the thickness is 5mm. High purity materials of Ge and Si single crystals were charged together into a fused-silica crucible. Boron (B) was added as a p-type dopant, and phosphorus (P) was added as an n-type dopant.

2.2 Measurement

High concentration Ge-doping in CZ-Si single crystals was measured mainly by WQF-410 Fourier transform infrared spectroscopy (FTIR) at room temperature (RT) and 10K together with the SEM-energy dispersive X-ray (EDX) spectroscopy[10], and part of the samples were examined by EDX spectroscopy and by secondary ion mass spectroscopy (SIMS) with a Philips XL30W/TMP. The electrical resistivity and conductivity type were determined by the four-point probe method with an ASTM-F84-84a.

The Seebeck coefficient was measured in the temperature range of 500～1100K. The specimens for measurements were grounded to a disk shape with a diameter in the range of 10～40mm, and the surface was cut to 5～30mm in thickness. The normal axis of the disks in single crystal was parallel along the growth direction. The Seebeck coefficient was measured by an apparatus which we designed and built. A schematic of the apparatus is shown in Fig. 1. The samples were held between two copper blocks in a flowing argon gas atmosphere. It has two probes made of a fine type K (Chromel/Alumel) thermocouple to detect the temperature on the copper surface. The electromotive force induced by the temperature difference of those blocks is detected by the potential difference meter. The Seebeck coefficient was estimated from the linear relationship between the electromotive force and the temperature difference. The measured Seebeck coefficient was not corrected by the Seebeck coefficient of the copper block, so it is the relative Seebeck coefficient.

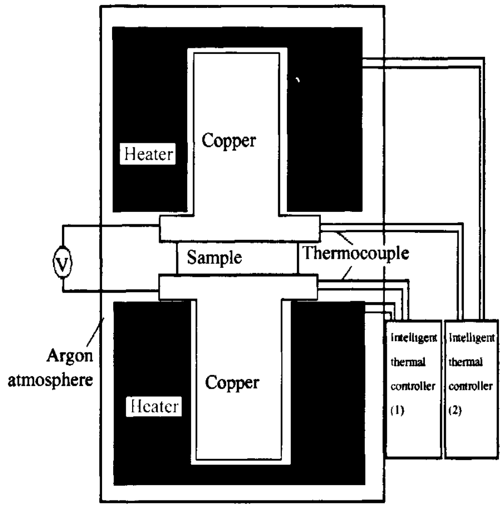

Fig. 1 Schematic of the Seebeck coefficient apparatus

3 Results and discussion

In this work, five samples were investigated. Table 1 shows the Seebeck coefficient of SiGe crystals with different Ge contents as a function of temperature. Sample 1 is an n-type poly-crystal with a Ge content of 20wt%. Sample 2 is an n-type single crystal with a Ge content of 0.5wt%. Sample 3 is an n-type free Ge CZ-Si single crystal.

Figure 2 shows the absolute value of the Seebeck coefficient of SiGe single crystals as a function of temperature. The higher curve is the Seebeck coefficient of SiGe alloy (5% Ge, p-type, called sample 4) with a 〈100〉 orientation as a function of temperature, and the lower curve is the Seebeck coefficient of SiGe alloy (5% Ge, p-type, called sample 5) with a 〈111〉 orientation as a function of temperature. Sample 1 is poly-crystal, and other samples are single crystals. We can

Table 1 Seebeck coefficient of SiGe crystals with different Ge contents against the temperature

Temperature/K		600	700	740	800	930	970	1040	Average
Seebeck coefficient at different Ge contents/(mV/K)	20% Ge n-type	0.57364	0.55615	0.77250	1.39867	0.43753	0.28062	9.14185	0.59436
	0.5% Ge n-type	0.43658	0.67737	0.51259	0.35005	0.21	0.13254	0.098154	0.34533
	0% Ge n-type	0.25179	0.6164	0.67810	0.66101	0.53747	0.25786	0.10467	0.31263

draw the following conclusions from Fig. 2. First, the Seebeck coefficient depends on temperature, which shows a maximum around 730K. Second, nearly all the Seebeck coefficients of ⟨100⟩ are larger than those of ⟨111⟩ at the same temperature.

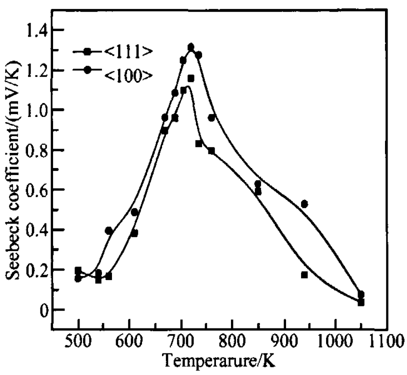

Fig. 2 Seebeck coefficient of CZ-SiGe (Ge 5wt% p-type) single crystals with ⟨111⟩ and ⟨100⟩ orientations against the temperature

Figure 2 and Table 1 show that all the samples have a maximal Seebeck coefficient. Nearly all of the maximal Seebeck coefficients are in the temperature range of 700 ~ 900K. With raising temperature, especially beyond 900K, the Seebeck coefficient decreases in SiGe alloy. This phenomenon may originate in the effect of thermal excitation of carriers across the gap from the conduction band.

From each sample's average Seebeck coefficient, we can see the relationship between Seebeck coefficient and composition. The Seebeck coefficient increases with increasing Ge content in the composition range we investigated.

4 Summary

Heavily impurity-doped single crystals of SiGe alloy with different compositions were grown by the Czochralski technique. The Seebeck coefficients of the grown alloy were investigated in the temperature range of 500~1100K with an apparatus designed and built in our laboratory. The Seebeck coefficient of SiGe single crystal depends greatly on the temperature. All the samples have a maximal Seebeck coefficient in the temperature range of 700~900K. In the samples investigated, the Seebeck coefficient increased with increasing germanium content. The Seebeck coefficient of the samples with ⟨111⟩ orientation is smaller than that of the samples with ⟨100⟩ orientation at the same temperature.

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直拉 SiGe 合金的高温 Seebeck 系数*

索开南[1,†]　张维连[1]　牛新环[2]　蒋中伟[1]

(1 河北工业大学半导体材料研究所，天津　300130)
(2 河北工业大学微电子技术研究所，天津　300130)

摘要： 为了更好地发掘 SiGe 合金的热电转换性能的潜力，对几组不同的 SiGe 合金样品进行了性能测试，主要是对不同参数样品的 Seebeck 系数值进行对比，从而得出热电性能的最佳组合．不仅比较了不同组分、不同晶向和不同导电类型样品的 Seebeck 系数，还对单晶 SiGe 合金和多晶 SiGe 合金的热电性能进行了对比分析．发现 SiGe 合金的 Seebeck 系数具有明显的各向异性，〈100〉晶向的 Seebeck 系数明显优于〈111〉晶向．Seebeck 系数与测试温度具有非常密切的依赖关系，随着温度的变化所有样品均在 700～900K 的温度范围内出现了峰值．此外还对 SiGe 合金的 Seebeck 系数与组分的关系进行了详细描述．

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† 通信作者．Email：suokainan211@sohu.com
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