Materials Science in Semiconductor Processing 88 (2018) 239–249

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Enhancing thermoelectric properties of *p*-type SiGe alloy through optimization of carrier concentration and processing parameters

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ARTICLE INFO

Keywords:
Thermoelectric
SiGe
p-type
Boron concentration
Melt spinning
Spark plasma sintering

ABSTRACT

The enhancement in thermoelectric (TE) properties of *p*-type SiGe alloys through the optimization of carrier concentration and processing parameters was reported. The *p*-type $Si_{80}Ge_{20}B_x$ alloys were prepared by melt spinning (MS) followed by spark plasma sintering (SPS). The effect of B concentration and processing parameters (rotating speed of Cu wheel in MS and holding time in SPS) was investigated. By adjusting the B content, the carrier concentration was notably changed but the carrier mobility was not significantly different. Consequently, TE properties were varied with B concentration and showed the optimum value for $Si_{80}Ge_{20}B_{0.5}$ with the maximum *ZT* of 0.71 at 1073 K. Increasing the Cu wheel rotating speed resulted in the refined microstructure of the MS ribbons. The smaller grain sizes were maintained even after SPS. However, despite the refined grains, the TE properties were insignificantly different for any rotating speed. Reducing the SPS holding time resulted in bulk samples with lower density, presumably containing nano/micro porous structure. The presence of pores in the microstructure effectively reduced thermal conductivity due to a stronger phonon scattering, but also suppressed the electrical contribution making an obvious drop in the power factor. The optimized holding time for SPS was 5 min at 1323 K.

1. Introduction

Thermoelectric (TE) devices can directly convert heat into electricity. Typically, they consist of semiconducting materials (*n*-type and *p*-type) connected in series. A thermoelectric conversion efficiency of each material is determined by the dimensionless figure-of-merit, *ZT*, which is given by the equation $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the thermal conductivity.

Although there is no theoretical upper limit for *ZT* values, the *ZT* of 1 is considered as the benchmark in the TE community [1,2], and is the value of the best TE materials used in present TE devices [3]. At present, the conventional TE materials around room temperature (RT) and mid-range temperature are Bi_2Te_3 and PbTe-related alloys, respectively [4–6]. For higher temperature range, SiGe alloys are one of the candidates due to their chemical stability and good TE properties at high temperature. In fact, the $Si_{80}Ge_{20}$ system has been used in Radioisotope TE Generators (RTGs) in NASA spaceships since 1970s (with $ZT \sim 0.5$ for *p*-type and ~ 0.9 for *n*-type at 1073 K) [7].

SiGe alloys are one of the most widely studied TE materials. Particularly in recent years, several studies have demonstrated the advanced improvement in *ZT* values of the SiGe system via nanostructuring approach. Nanostructures offer a material with complex crystal structures including high density of grain boundaries (nanostructured structure) [8–12], nanoparticles embedded in a matrix phase [13–17], modulation-doping in nanocomposites [18,19], and nanoscale defect features [20]. The main advantage of using SiGe nanostructure is the difference in the mean free path (MFP) between the electronic and phonon contributions (MFP of electron and phonon are ~ 5 nm and ~ 200–300 nm, respectively [11,21]). Therefore, nanostructuring approach in the scale range of 10–100 nm has a major influence to lattice thermal conductivity (κ_{lat}) but shows almost no effect on electrical transport. Such complex structures have been proven experimentally in which various effective phonon scattering mechanisms were introduced, leading to a drastic reduction of κ_{lat}. For instance, Basu et al. reported the improved TE performance of hot pressed nanostructured *n*-

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https://doi.org/10.1016/j.mssp.2018.08.020
Received 3 May 2018; Received in revised form 3 July 2018; Accepted 19 August 2018

type SiGe bulk alloys with κ approaching 0.9 $W\,m^{-1}\,K^{-1}$ and very high ZT of ~ 1.84 at 1073 K [8]. Bathula et al. dispersed SiC nanoparticles in the n-type SiGe matrix and observed the lowest κ of 1.9 $W\,m^{-1}\,K^{-1}$ yielding a high value of $ZT \sim 1.7$ at 1173 K [13]. Ahmad et al. used the nanocomposite approach by introducing YSi_2 nanoinclusions in p-type SiGe alloys. With proper amount of YSi_2 nanoinclusions, the κ was reduced by 62%, resulting in 34% improvement of ZT (~ 1.81 at 1100 K) [14].

In the synthesis of SiGe nanostructured alloys, most experimental works employed a solid state ball milling method [8–16,18–20]. Although this method is simple and can provide powders in nanoparticle size, it also has several drawbacks, such as a long milling time (up to > 90 h) [8,9,20], contamination from the grinding media, or proneness to oxidation during the process. The contamination from the grinding media, e.g. yttria stabilized zirconia (YSZ), could lead to a significant reduction in electrical conductivity and hence lower ZT [22]. Similarly, oxidation of SiGe alloys or the formation of SiO_2 nanoinclusion could have a deteriorate effect on the TE properties [23–25]. On the other hand, melt spinning (MS) is a powerful technique for fabrication of homogeneous alloy. It is one of the rapid solidification techniques that play an important role in preparation of many advanced functional materials [26]. The process is much faster than ball milling and provide negligible contamination or oxidation. It has been demonstrated to fabricate many TE materials with improved TE properties, for example, Bi_2Te_3 [27], skutterudite $CoSb_3$ [28], and several Si-silicide systems [29–32].

In this work, we demonstrated the fabrication of p-type SiGe alloys (boron doped) by using the MS technique in combination with spark plasma sintering (SPS). Researching through literatures, it was hardly found reports on the variation of B concentration on the change in TE properties of SiGe alloys [24,33]. In addition, the processing parameters in the MS [30,31] and SPS processes [20,25] for the fabrication of SiGe alloy were rarely reported. Therefore, in the present research, the effect of boron concentration as well as processing parameters on the microstructure and TE properties were systematically investigated. Under the optimization condition, it was found that the TE properties of the p-type SiGe alloys were significantly improved.

2. Experimental procedure

Firstly, we investigated the effect of B concentration on the TE properties of SiGe alloys prepared by melt spinning (MS) and spark plasma sintering (SPS). A series of ingot samples with nominal compositions of $Si_{80}Ge_{20}B_x$ (x = 0.1, 0.23, 0.5, 1.0, 1.5, 3.0) were prepared by arc melting (AM) from high-purity Si chunk (11 N), Ge shot (3 N) and B chunk (99.9%) in a vacuum chamber under Ar atmosphere. Then, ribbon samples were prepared by melt spinning (MS) process. In this process, the obtained ingots were put into a boron nitride (BN) tube, with a 0.6 mm diameter nozzle, and melted by induction heating in Ar atmosphere. The 6-turn Cu coils in the space of 4 cm height and 3 cm width surrounds the BN tube. The inner diameter of the coil is 2 cm whereas the Cu wire diameter is 0.5 cm. The electrical power of 20 mA, 110 V, 60-Hz AC current was supplied to create induction heating. The molten alloys were ejected, with a pressure of 0.02 MPa, onto a Cu wheel (a radius of 10 cm) rotating at the speed of 2000 rpm. The gap between the nozzle and the wheel was 0.2 mm. The rapidly solidified ribbon samples were crushed manually into fine powders and placed into a high strength graphite die for fabricating bulk samples by SPS. The ramp rate for the SPS processing was 48 °C/min. The SPS process was controlled at 1323 K for 5 min in an Ar atmosphere under an axial pressure of 100 MPa. The $Si_{80}Ge_{20}B_x$ bulk samples in this stage were ready for microstructural and properties investigation.

Secondly, for the processing parameter optimization, the sample with the best TE properties from the first experiment was chosen. Two parameters were under investigation: the rotating speed of the Cu wheel, and the SPS holding time. The first parameter could change the crystallite size of the samples, and thus possibly improved TE properties. The rotating speed was adjusted between 2000 rpm and 6000 rpm. The SPS holding time also had an effect on the density and microstructure, and again, could enhance the TE properties. The SPS holding times used in this experiment were varied from 3 min to 7 min.

Phase and crystallographic structure were investigated using powder X-ray diffraction (XRD, Rigaku, Ultima IV) analysis using Cu K_α radiation. The microstructures of the ribbon surfaces and finely polished bulk sample surfaces were investigated under field emission scanning electron microscopy (FE-SEM; JEOL JSM-6500F). A carrier concentration (n) and carrier mobility (μ) were measured using the Hall coefficient measurement system (Toyo Resitest8340) at room temperature under a magnetic field of 0.5 T. The thermal conductivity (??) was calculated by using the equation $\kappa = DdC$, where d is the bulk density and C is the heat capacity of which the literature value was used [6]. The thermal diffusivity D was measured by a flash diffusivity method in the Netzsch LFA467 instrument from room temperature (RT) to 1073 K under an Ar atmosphere. Seebeck coefficient and electrical conductivity of the samples were measured by the commercial system (Ulvac-Riko, ZEM-3) from RT to 1073 K in a He atmosphere.

3. Results and discussion

3.1. Optimization of B concentration

Fig. 1 shows the powder XRD patterns of the p-type $Si_{80}Ge_{20}B_x$ (x = 0.1, 0.23, 0.5, 1.0, 1.5, 3.0) samples after SPS. All of the XRD peaks agree well with the literature data (JCPDS:00-005-0565) and [13,20,34], without any impurity phases, indicating the single phase of $Si_{80}Ge_{20}B_x$. However, the asymmetric XRD peaks were observed, particularly for x = 0.1 and 0.23. Usually, the asymmetric XRD peaks can occur from several causes, such as two phases, stacking fault, concentration gradient, dislocation, or strain. In our case, we believe that it could be due to strain contribution since the larger atoms of Ge were substituted for Si in these alloys. The addition of B with smaller size atoms can accommodate the strain. Thus the asymmetric peaks are reduced for increasing B content. The lattice parameters (a) calculated from these XRD patterns are summarized in Table 1, which shows that the a value is relatively the same for every sample (about

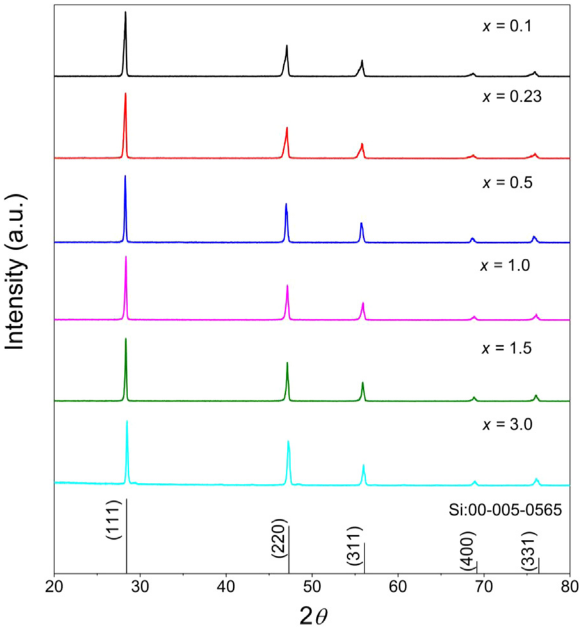

Fig. 1. Powder XRD patterns of the $Si_{80}Ge_{20}B_x$ (x = 0.1, 0.23, 0.5, 1.0, 1.5, 3.0) bulk samples.