Fabrication and Evaluation of Graded (Si-MoSi₂)/SiGe Thermoelectric Materials by HIP Sintering

J. S. Lin and Y. Miyamoto

Joining & Welding Research Institute, Osaka University, Ibaraki 567, Osaka, Japan

H. Kido

Osaka Municipal Technical Research Institute, Morinomiya, Jhoto-Ku 563, Osaka, Japan

Based on the concept of functionally graded materials, the thermoelectric conversion unit of SiGe with graded electrodes was designed and fabricated by HIP sintering process in order to obtain a good electrical and mechanical contact. The composite of Si and MoSi₂ was used as the electrode, and the effect of the MoSi₂ volume fraction on the electrical resistivity was studied. The results show that the electrical resistivity decreases exponentially with increasing MoSi₂ content and reaches the order of $10^{-4} \Omega \cdot \text{cm}$ when the volume fraction of MoSi₂ was beyond 25%. The graded (Si-MoSi₂)/SiGe obtained has dense microstructures and well bonded interfaces. The electrical resistivity continuously decreased from the SiGe to the surface electrode in the zone of graded structure.

[thermoelectric conversion, electrical resistivity, functionally graded material, HIP sintering, microstructure]

1. Introduction

For high temperature use of the thermoelectric conversion (TEC) device around 800 °C, *p* and *n*-type SiGe are available materials. They are connected to high and low temperature electrodes by normal joining techniques. However, the considerable mismatch of the thermal expansion between the electrode and SiGe ($\sim 3.7 \times 10^{-6}/\text{K}$) often results in a deterioration of the mechanical and/or thermoelectric properties at the joined interfaces. In our former work [1], a one-step sintering process was developed to fabricate the TEC cell with its electrode. Undoped SiGe and (Si-MoSi₂) composites were used for the TEC cell and the electrode, respectively. The results showed that this process can substitute for the joining process of the SiGe cell and electrodes. The residual stress in the unit can be effectively relaxed by using a graded structure of (Si-MoSi₂). The addition of MoSi₂ into the Si matrix considerably reduced the electrical resistivity and controlled the thermal expansion mismatch between the Si and SiGe.

In the present work, the variation of the electrical resistivity with the volume fraction of MoSi₂ in the Si matrix has been studied. SiGe doped with boron and phosphorus and its electrodes of (Si-MoSi₂) were sintered in one step by HIP process. The electrical resistivity, carrier concentration and mobility of the TEC unit were evaluated.

2. Experimental Procedure

Commercial powders of MoSi₂, Si and Si_{0.8}Ge_{0.2} with nominal sizes of 1.09 μm , 20 μm and 10 μm were used as raw materials. The *p* and *n*-type SiGe were obtained by doping with 0.2 at.% boron and 0.3 at.% phosphorus, respectively. The powders in pre-determined volume fractions were mixed in ethanol for over 48 hours, dried in a vacuum furnace. The compositionally graded (Si-MoSi₂)/SiGe green compact was vacuum sealed into a glass capsule with BN powder bed, and then sintered at 1250 °C for 45 minutes under an Ar gas pressure of 100 MPa.

The electrical resistivity was determined by the four-probe method, the carrier concentration and mobility were determined

by measuring the Hall coefficient of SiGe at room temperature. The microstructure of the specimen was observed by using a scanning electron microscope (SEM).

Results and Discussion

Effect of MoSi₂ volume fraction on electrical resistivity

Silicon has good thermal conductivity (1.5 W/cm·K at 273K) and low thermal expansion coefficient ($2.5 \times 10^{-6}/\text{K}$); MoSi₂ has low electrical resistivity ($2 \times 10^{-2} \Omega \cdot \text{cm}$). The electrical properties of the (Si-MoSi₂) composite are expected to be dependent on the volume fraction of MoSi₂. Its electrical resistivity is shown in Figure 1. In the case of MoSi₂ free, the electrical resistivity is about $1.5 \times 10^{-1} \Omega \cdot \text{cm}$, and as the volume fraction of MoSi₂ increases, it decreases exponentially to the order of $10^{-4} \Omega \cdot \text{cm}$. This behavior is clearly understood by the microstructural observation of the samples. At low MoSi₂ content, there are no low resistance current path (Figure 2(a)). As increasing the MoSi₂ content, its grains are completely connected each other as seen in Figure 2(b), forming a good conductive path.

Figure 1. Effect of MoSi₂ volume fraction on the electrical resistivity of the Si-MoSi₂ composites.

Figure 2. Microstructures in the (Si-MoSi₂) composites with 15 vol% MoSi₂ (a) and 30 vol% MoSi₂ (b).

Fabrication and microstructures

The graded (Si-MoSi₂)/SiGe unit was designed as shown in Figure 3. The surface layer consists of 25 vol% MoSi₂ and 75 vol% Si. Because of the high thermal expansion coefficient of MoSi₂ ($8.3 \times 10^{-6}/K$), an excess of MoSi₂ will lead to a large mismatch in thermal expansion between the electrode and SiGe although the electrical resistivity can be lowered. Based on the finite element analysis on the thermal residual stresses in this structure [1], a linear variation of the thermal expansion coefficient was constructed from the SiGe to the surface layer in order to obtain an optimum distribution of internal stress. The second and third layers made up of SiGe with 10 and 5 vol% MoSi₂, respectively. The addition of MoSi₂ in SiGe matrix can ensure that the electrical resistance decreases continuously from the SiGe to the surface electrode with satisfaction of the requirement of the thermal expansion mismatch.

Figure 3. Structure of the sample.

The SEM microstructures in the vicinity of interfaces are illustrated in Figure 4. The microstructures are distributed uniformly in every layer, and the interfaces between every two neighbor layers are well bonded. The homogeneous sample of SiGe sintered in the same process had a density of 3.06 g/cm³, which was 99.6% of the theoretical density, 3.07 g/cm³.

Figure 4. SEM microstructures in the vicinity of every interfaces.

Electrical resistivity

The profile of the electrical resistivity in the (Si-MoSi₂)/SiGe TEC unit is shown in Figure 5. In the zone of doped SiGe, the resistivity shows the same values as reported from the powder manufacturer. In the zone of graded structures, the electrical resistivity decreases continuously from SiGe to the surface electrode, and reaches the minimum at about $4.0 \times 10^{-4} \Omega \cdot \text{cm}$.

Figure 6 illustrates some thermoelectric parameters of *p-n* type SiGe units joined with and without graded electrodes. For the carrier mobility in Figure 6(a) and carrier concentration in Figure 6(b), we can see that there is no remarkable difference between the SiGe units with and without the graded electrode. Moreover, the mobility and carrier concentration are almost

Figure 5. Profile of the electrical resistivity in (Si-MoSi₂)/SiGe (*p*-type) thermoelectric conversion unit.

constant near and far from the interface. For the electrical resistivity, the graded electrode joined-unit presents an excellent profile as compared with the directly joined unit. The latter shows a typical *p-n* contact resistivity at the interface, while the former joint gives a lower electrical resistivity than both type of SiGe in the zone of electrode. In addition, the profile of the resistivity after the heat treatment at 900 °C for 24 hours shows that such thermal exposure has no evident influence on the electrical resistivity as seen in Figure 6(c).

According to above results, it is expected that the SiGe thermoelectric conversion unit joined with graded (Si-MoSi₂) electrodes will possess excellent thermoelectric power.

4. Conclusions

The electrical resistivity of the (Si-MoSi₂) composites decreases exponentially with the increase of the MoSi₂ volume fraction. It can reach an order of 10⁻⁴ Ω·cm when MoSi₂ exceeds about 25% volume fraction.

The graded design of the electrode can provide a smooth profile of the electrical resistivity which decreases continuously from the SiGe to the surface electrode of (Si-MoSi₂). The graded structures have no evident influence on the carrier mobility and concentration in the zone near the interface.

Acknowledgment

This study was supported by the grants from Science and Technology Agency for Functionally Graded Materials and Nippon Sheet Glass Foundation for Materials Science and Engineering.

References

- [1] J. S. Lin, K. Tanihata, Y. Miyamoto and H. Kido, Fourth Int. Symp. on Functionally Graded Materials, October 21-24, 1996, Tsukuba, Japan, in printing.

Figure 6. The variation of the carrier mobility (a), carrier concentration (b) and electrical resistivity (c) as a function of the distance from the edge.