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Single crystalline β-$FeSi_2$ grown using high-purity $FeSi_2$ source

Kouhei Gotoh [a], Hirokazu Suzuki [a], Haruhiko Udono [a,*], Isao Kikuma [a], Fumitaka Esaka [b], Masahito Uchikoshi [c], Minoru Isshiki [c]

[a] Graduate School of Sci. and Eng., Ibaraki Univ., 4-12-1 Nakanaruwasa Hitachi, 316-8511, Japan
[b] Japan Atomic Energy Agency, Shirakata-Shirane 2-4, Tokai, Naka, Ibaraki 319-1195, Japan
[c] Inst. Multidisciplinary Research for Advanced Materials, Tohoku Univ., 1-1, Katahira 2, Aobaku Sendai 980-8577, Japan

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Abstract

We have investigated the effect of $FeSi_2$ source purity on the electrical property of β-$FeSi_2$ grown from solution. A high-purity $FeSi_2$ source avoided a contamination of Cu and W metals was synthesized by melting a high-purity Fe (5N) and Si (5N-up) in a quartz ampoule. Glow discharge mass spectrometry revealed that the purity of the $FeSi_2$ source synthesized using 5N-Fe and a quartz-ampoule-melting process is one order of magnitude higher than that of the conventional arc-melted $FeSi_2$ source using 4N-Fe. The β-$FeSi_2$ crystals grown using the high-purity $FeSi_2$ and Zn solvent showed n-type conduction, whereas those grown using the arc-melted $FeSi_2$ showed p-type. The carrier concentration of the n-type crystals was $(4.9–6.3)\times10^{18}$ cm^{-3}, which was more than 10 times higher than that of the p-type crystals (5.2×10^{17} cm^{-3}). From the ICP-MS and SIMS analysis of the grown crystals, we found that dominant impurity concentrations (Cr, Mn, Co, Ni, Cu, Zn and W) in the p-type crystals were higher than those in the n-type ones. Therefore, the p-type conductivity of undoped crystals grown using Zn solvent results from unintentional doping by the high impurity level of the used $FeSi_2$ source.

Keywords: β-$FeSi_2$; Single crystal; Solution growth; Hall measurement

1. Introduction

Semiconducting iron disilicide, β-$FeSi_2$, has been attracting much attention in recent years because of its technological potential in the field of optoelectronic and thermoelectric applications [1]. Since the successful electroluminescence (EL) from β-$FeSi_2$/Si structure [2], a lot of researchers have investigated the optical properties of β-$FeSi_2$ to clarify the luminescence mechanism [3–8]. However, the luminescence mechanism has not been clearly understood, so far.

One of the interesting facts is that most of luminescence is observed from thin film or precipitate β-$FeSi_2$ [9,10]. Recently, Udono et al. observed the photoluminescence from solution grown β-$FeSi_2$, but the intensity is very weak [11]. In order to progress the understanding of the luminescence mechanism of β-$FeSi_2$, it is necessary to prepare bulk β-$FeSi_2$ single crystal with high-crystalline quality and high purity.

A purity of iron source is significant issue for the crystal growth of β-$FeSi_2$ because metal impurity in Fe source affects the electrical property of the crystal. Heinrich et al. and Behr et al. reported that the conduction type of chemical vapor transport (CVT) grown crystal changes from p-to n-type when the Fe source changes from 4N- to 5N-grade [12,13]. In the solution growth using Zn solvent and 4N-grade Fe source, p-type crystal ($p\sim4\times10^{17}$ cm^{-3}) is usually grown [14]. However, the origin of its p-type carrier is not clearly understood, so far. In this paper, we report the synthesis of high-purity $FeSi_2$ alloy source and the solution growth of β-$FeSi_2$ using Zn (6N) solvent and the synthesized high-purity $FeSi_2$ source.

2. Experimental

A high-purity $FeSi_2$ alloy ingot was synthesized from the melt using a siliconit furnace. A certain amount of silicon (5Nup) and iron (5N) [15] was enclosed in a purified quartz ampoule under a high vacuum ($<5\times10^{-6}$ Torr). The ampoule was heated at 1350 °C for 10 min and then cooled. The composition ratio of Si/Fe was changed between 1.5 and 2.5 to

* Corresponding author. Tel./fax: +81 294 38 5126.
E-mail address: udono@mx.ibaraki.ac.jp (H. Udono).

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examine the influence of the source composition on the electrical properties of β-$FeSi_2$. Concentration of impurities in the synthesized $FeSi_2$ ingot was analyzed by induced coupled plasma mass spectrometry (ICP-MS) and glow discharge mass spectrometry (GDMS). We also measured an arc-melted $FeSi_2$ source, which was usually used as a solute in our previous solution growth and was synthesized by conventional arc-melting method from Fe (4N) and Si (5Nup) as a comparison.

Crystal growth of β-$FeSi_2$ was carried out by the temperature gradient solution growth method using Zn (6N) solvent and the high-purity $FeSi_2$ or the arc-melted $FeSi_2$ source. Details of the growth procedure are descried in the literatures. Precise growth conditions are listed in Table 1, where T_G and T_S indicate the temperature at growth part and $FeSi_2$ source part, respectively.

Characterization of the grown crystals was performed by an optical microscope, a scanning electron microscope (SEM) with an energy dispersive X-ray microscopy (EDX) and an X-ray diffraction. The electrical property of the grown crystals was measured by the Hall effect measurement. Impurity concentrations in the crystals were evaluated by the inductively coupled plasma mass spectroscopy (ICP-MS) and secondary ion mass spectroscopy (SIMS) for the mass of grown crystals and each crystal, which was used as the Hall measurement, respectively.

3. Results and discussion

3.1. Synthesize of high-purity $FeSi_2$ ingot

Fig. 1 (a) and (b) show microphotographs of a typical high-purity $FeSi_2$ alloy ingot synthesized from 5N-Fe and 5Nup-Si by the quartz-ampoule-melting method. The surface on the as-synthesized ingot is a metallic luster. Cross sectional observation revealed that the ingot had no void or crack as shown in Fig. 1 (b). Fig. 2 shows a SEM image on the cross sectional surface of $FeSi_2$ ingot. The ingot contained only ε- and α-phase with their stoichiometric composition. Thus, it is confirmed that the ingot was melted homogeneously. We measured the impurity concentration of the high-purity $FeSi_2$ ingot and arc-melted $FeSi_2$ ingot by the GDMS. The results are listed in Table 2. From the table, we found that the concentration of impurities in the high-purity $FeSi_2$ decreased by one digit or more compared with arc-melted $FeSi_2$. The total purity of both $FeSi_2$ ingots was 99.947% for the arc-melted $FeSi_2$ and 99.997% for the high-purity one. Thus, it is clear that high-purity $FeSi_2$ source is able to obtain by the quartz-ampoule-melting process. The concentration levels of most of the elements were the same as those in 4N-Fe and 5N-Fe except for

Table 1
Growth conditions of β-$FeSi_2$ single crystals, The "Q-melt" and "A-melt" mean the quartz-ampoule-melting method and the arc-melting method, respectively

No.	$FeSi_2$ source synthesis	(Si/Fe)	T_G [°C]	T_S [°C]	Periods [h]
#1	5N-Fe, Q-melt	1.5	850	905	504
#2	5N-Fe, Q-melt	2.0	870	920	504
#3	5N-Fe, Q-melt	2.5	855	900	504
#4	4N-Fe, A-melt	2.0	885	925	336

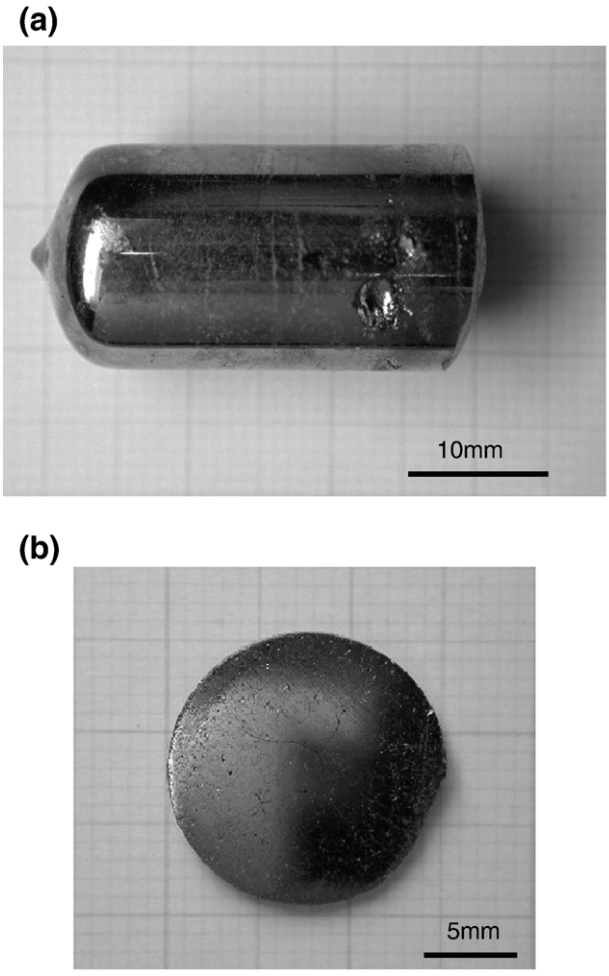

Fig. 1. (a) High-purity $FeSi_2$ ingot; (b) Cross sectional image of as-polished high-purity $FeSi_2$ ingot.

W and Cu impurities, i.e., the significant concentration of the elements, such as P, Ni, Al, Cr and Mn in the arc-melted $FeSi_2$ would be due to the impurity in 4N-Fe source. On the other hand, a large amount of W and Cu impurities was detected in the

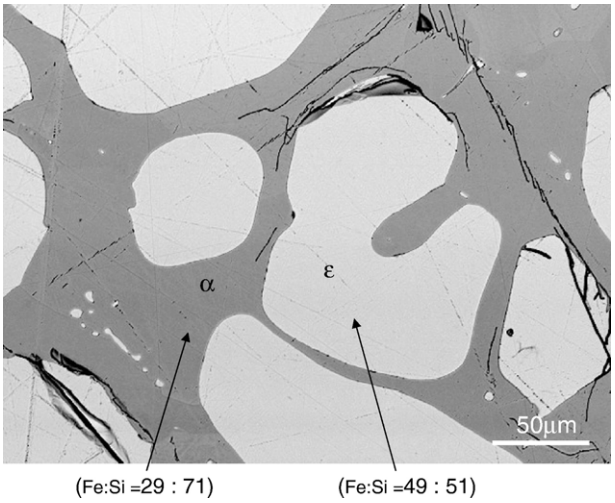

Fig. 2. Cross sectional SEM image of the high-purity $FeSi_2$ ingot.