Growth of bulk single crystals b-FeSi$_2$ by chemical vapour deposition

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Abstract Bulk single crystals β-FeSi$_2$, as a new photoelectric and thermoelectric material, has been successfully grown using chemical vapor transport technique by using iodine as transport agent in a sealed ampoule. The effects of crystal growth condition on quality and morphologies of the single crystals were studied. Both needle-like and grain-like single crystals were gained. By changing substrate temperature, tetrahedral high quality α-FeSi$_2$ single crystals were also obtained.

Keywords: b -FeSi$_2$ single crystals, a -FeSi$_2$ single crystals, chemical vapor transport.

Three kinds of structure of iron-silicides (FeSi$_2$) have been found[1,2]. One of them is the tetragonal type α-FeSi$_2$ with lattice constants of $a = b = 0.2695$ nm, $c = 0.509$ nm, which forms at above 980℃ and exhibits metallic behavior. The second type iron-silicide is β-FeSi$_2$ which has semiconductive characteristic and orthorhombic structure of the lattice constants of $a = 0.9879$ nm, $b = 0.7799$ nm and $c = 0.7839$ nm[1]. The γ-FeSi$_2$ with cubic structure is the third one that has lattice constant of $a = 0.5428$ nm[2].

Among the above three kinds of FeSi$_2$ phases, β-FeSi$_2$ exhibits potential application due to some properties. For example, one can obtain p-type semiconductor by doping Al and n-type by doping Co. β-FeSi$_2$ with strong infrared absorption is also a perfect photoelectric material. In addition, β-FeSi$_2$ possesses higher thermoelectric coefficient[3—5].

Several methods have been developed for β-FeSi$_2$ preparation such as sintering, molecular beam epitaxial growth and reactive deposition epitaxy. However, it is difficult to identify its crystallography parameters and properties due to the influences of surface effect, grain boundary and defect. Therefore, preparation of β-FeSi$_2$ single crystals becomes of importance in the measurement of its accurate physical properties.

In the middle 1990s, the needle-like β-FeSi$_2$ single crystals were firstly grown via the process of chemical vapor transport, and the physical properties of the bulk β-FeSi$_2$ crystal were measured by Kloc[1]. It was found that, at low temperature (32 K), heavy electrons show the mobility of m_n =

48 $cm^2 V^{-1} s^{-1}$ that is ten times as high as that of polycrystalline β-$FeSi_2$; and the mobility of holes m_p in the p-type crystal reaches a maximum of 1200 $cm^2 V^{-1}s^{-1}$ at 67 K, which is 25—50 times larger than that of published results. These results indicated the importance of obtaining high quality β-$FeSi_2$ single crystal. In this paper, technique and method for β-$FeSi_2$ single crystal preparation were studied and two single crystals with different shape were successfully gained.

1 Experimental methods

$FeSi_2$ single crystals have been grown by chemical vapor transport technique. In the preparation, I_2 was used as the transport agent in a sealed ampoule. High pure Fe (>99.9%) and Si (>99.999%) were firstly mixed by arc-melting in the high vacuum. An extra 4% silicon above the stoichiometric amount was added to compensate for volatilization of silicon during the melting. The vapor phase growth was carried out in quartz ampoules, which have the dimensions of ϕ15 mm×150 mm and ϕ25 mm×200 mm. The Si (111) was used for substrate. Fig. 1 shows the schematic of the growth ampoule. Since position 2 was linked to the vacuum system, it was sealed after the ampoule was evacuated to 10^{-6} Torr, then the ampoule was shaken to crack the iodine-containing capillary so that heated iodine completely vaporized into the ampoule. The second encapsulation was done at position 1. The sealed ampoule was finally put in a temperature gradient furnace to carry out crystal growth. The experiment conditions are shown in table 1.

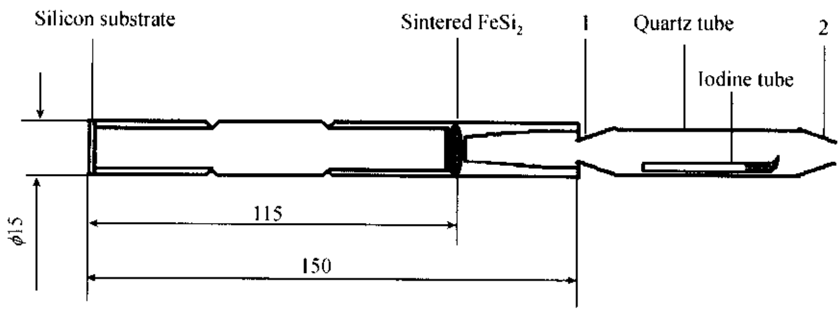

Fig. 1. The schematic of ampoule.

Table 1 Different experiment conditions for β-$FeSi_2$ crystal growth

Sample	Substrate temperature/℃	Source temperature/℃	Growth time/h	Ampoule size/mm
1	750	1050	8	ϕ15×150
2	950	1050	11	ϕ15×150
3	750	1050	648	ϕ25×200

2 Results and discussion

Fig. 2 shows X-ray pattern of β-$FeSi_2$ single crystal obtained under the condition of 750℃ for 8 h on Si substrate. It can be seen that β-$FeSi_2$ crystalline co-existed with Si. Fig. 3 shows typical morphology of the single crystal grown on Si substrate. Analysis of EDAX indicated that the component of the crystal is Fe/Si = 1∶2. The morphologies of crystal are regular shape, but the crystals shown in fig. 3(a) possess rhombic-tetrahedron structure while fig. 3(b) rhombic-cone structure.

Fig. 4 presents X-ray pattern of specimen that grows at 950℃ for 11 h. Except a peak of diffraction Si, the others are all α-$FeSi_2$ crystal, indicating the deposition is α-$FeSi_2$. We found there is a big difference between the α-$FeSi_2$ and β-$FeSi_2$ morphology. The α-$FeSi_2$ crystal always has tetrahedral shape as shown in fig. 5. Our

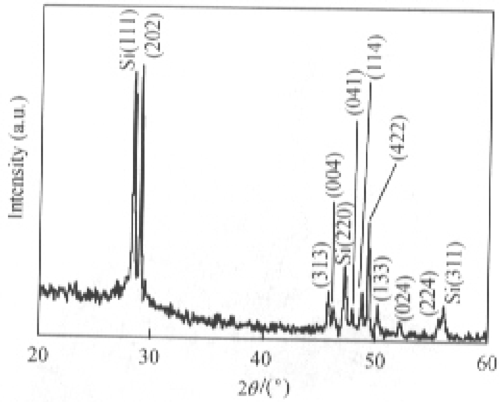

Fig. 2. X-ray pattern of β-$FeSi_2$ (substrate temperature 750 ℃ for 8 h).

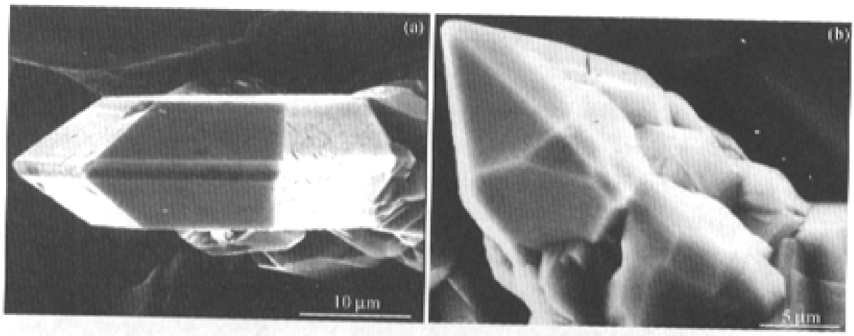

Fig. 3. SEM image of β-$FeSi_2$ (substrate temperature 750℃ for 8 h).

experiment results confirm that α-$FeSi_2$ crystals grow at high temperature, and can be gained by lowering temperature, no β-$FeSi_2$ can be found in the ampoule.

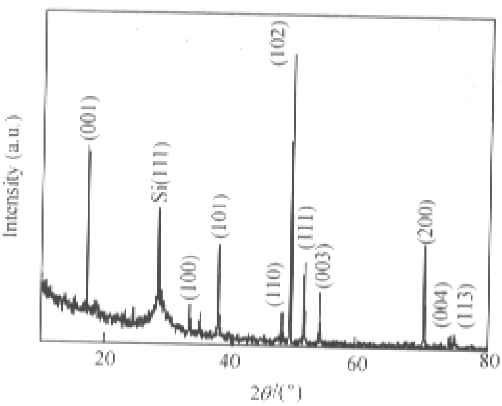

Fig. 4. X-ray pattern of α-$FeSi_2$ (substrate temperature 950 ℃ for 11 h).

These results indicated, even at the same source temperature, different substrate temperatures lead to different kinds of the crystals: α-$FeSi_2$ phase can be gained at 950℃, while β-$FeSi_2$ phase at 750℃. Although α-$FeSi_2$ is high-temperature metastable phase, it does not transform into β-$FeSi_2$ phase with the furnace cooling. This implies that α-$FeSi_2$ is thermodynamically metastable at ambient temperature, but it does not easily undergo a phase transition from α-$FeSi_2$ to β-$FeSi_2$.

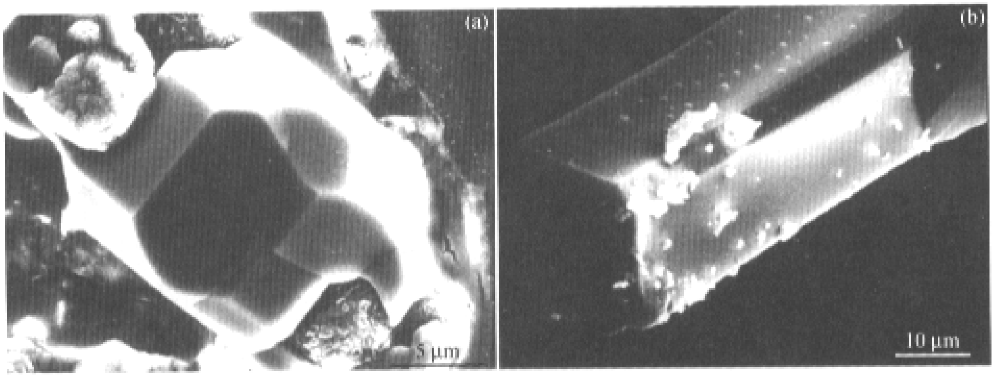

Fig. 5. SEM image of α-$FeSi_2$ (substrate temperature 950℃ for 11 h).

In order to gain single crystal with the large size, the ampoule and the growth time were enlarged. In our experiments, time was extended to 648 h. Large needle-like β-$FeSi_2$ single crystal was found on the wall of the ampoule (fig. 6(a)). The largest one is about 10 mm in length. The grain-like β-$FeSi_2$ single crystal was firstly obtained (fig. 6(b)). The structure analysis demonstrated that lattice parameters of needle-like single crystal are a = 0.7803 nm, b = 0.7837 nm, c = 0.9878 nm, while of grain-like single crystal are a = 0.7796 nm, b = 0.7826 nm, c = 0.9866 nm. The integrality of single crystal with gain shape is better than that with needle shape.

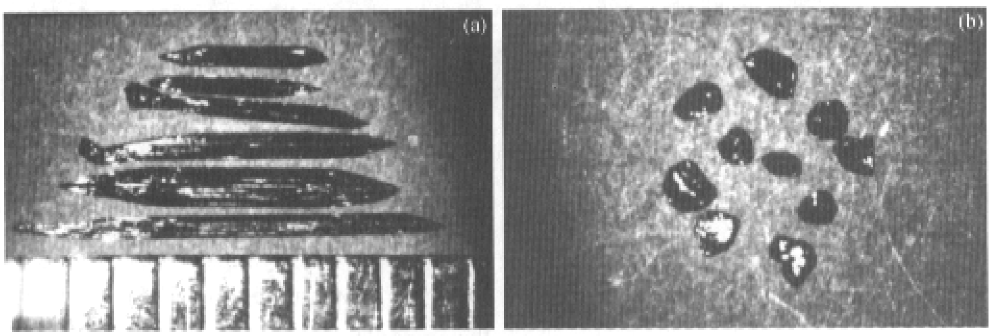

Fig. 6. SEM images of β-$FeSi_2$ single crystals grown on ampoule wall (substrate temperature 750℃ for 8 h).

Since deposited crystals are anomalous when single crystals are pure silicon, we suggested that single crystals might nucleate and grow on deposited silicon (see fig. 7). By careful observing, we found that one end of β-$FeSi_2$ single crystals was sharper, indicating that single crystalline grew from one end to the other end. The growth speed of c-axial is about 10 times that of a- and b-axial.

3 Conclusion

By chemical vapor transport technique with iodine as the transport agent, bulk β-$FeSi_2$ single crystals have been grown in a sealed ampoule. It was found that β-$FeSi_2$ can be obtained at substrate temperature of 750℃, while α-$FeSi_2$ at 950℃. Both needle-like and grain-like β-$FeSi_2$ single crystals were gained in the present study. The growth morphology of grain-like β-$FeSi_2$ single crystal is better than that of needle-like crystal indicating that grain-like β-$FeSi_2$ single crystal may be the best candidate for better understanding its accurate physical properties.

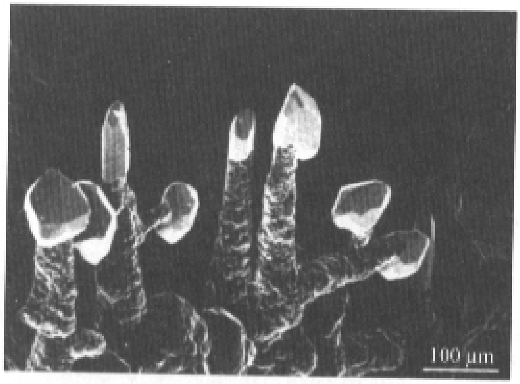

Fig. 7. SEM image of β-$FeSi_2$.

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