Heat Capacity study of $\beta$-FeSi$_2$ single crystals

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Abstract

Heat Capacity of needle-like [length=5mm, diameter=1 mm] $\beta$-FeSi$_2$ single crystal, grown by chemical vapor transport has been measured. Two anomalies are found, a broad deviation centered around 160 K and a clear deviation at a temperature of 255 K approximately. We have attempted to relate these to the anomalies previously reported in the case of the resistivity data. The Transient Thermoelectric Effect [TTE] results lead us to the inference that the system undergoes from single carrier system to at least two carrier system at 220 K-our heat capacity results seem to provide further independent evidence for this transition in this system.
1 Introduction

Among the silicides $\beta$-FeSi$_2$, a semiconductor, is an interesting and promising material for several reasons. Broadly speaking $\beta$-FeSi$_2$ is environmentally friendly, and it is also compatible with existing silicon technology. From the technological point of view the photoelectric properties of this and related materials may be utilized in optoelectronic devices that can be integrated into silicon technology. Silicon dominates the microelectronics industry. However silicon is a poor emitter of light due to its indirect band-gap, this leads to efficiencies of 0.01-0.1% even for complex silicon based LED structures. Thus there are many efforts to remedy this situation. In this regard semiconducting silicides[3] offer several advantages. In particular, Iron disilicide $\beta$-FeSi$_2$ is a promising material for optoelectronic applications plus it is as already mentioned it is environmentally friendly or Kankyo semiconductor. Specifically it emits light at 1.55 $\mu$m [0.8 eV] which is the value required for SiO$_2$ optical fiber communications. However there are some hurdles in fabricating $\beta$-FeSi$_2$ films on Si-substrates using Molecular Beam Epitaxy. The diffusion of iron into Si substrate is perhaps the most difficult to overcome. In short $\beta$-FeSi$_2$ is attractive as potential constituents in optical and thermoelectric devices. But, a main problem remains that the semiconducting and physical properties are very sensitive to sample preparation [5, 6]. Yet another issue is that band calculations suggest a strong coupling between band edge states to the lattice [7], implying low carrier mobility. In contrast, magneto-transport experiments [8] indicate the existence of high mobility carriers in addition to the ones with low mobility. Recently Hara et al.[9] reported a ”phase-transition” around 220 K based on resistivity data.

In this paper we report on our experimental measurements of the heat capacity of needle-like single crystal of $\beta$-FeSi$_2$, grown by chemical vapor transport method [10]. We find an anomaly at 255 K in the heat capacity data, which provides support to resistivity transport data. There also seems to be another ”anomaly” at lower temperature of 100 K. From the Transient Thermoelectric Effect [TTE] results we can infer that the system under goes from single carrier system to at least two carrier system at 220 K [9].

2 Experimental

Needle-like single crystals of $\beta$-FeSi$_2$ were grown by chemical vapor transport [CVT] method [10]. The sample preparation is made from the gas phase, using iodine as a carrier gas, single phase needle-like $\beta$-FeSi$_2$ bulk crystals are obtained, with typical dimensions 5-10 mm length and 1mm diameter. The $\beta$-FeSi$_2$ needle-like crystal used in heat capacity experiment is shown in Fig. 1. The approximate dimensions of the crystal are 5mm length and 1mm diameter. The measured value of the mass was 1.26 ±0.01 mg.

The Heat Capacity [HC] was measured using Quantum Design Physical Property Measurement System [PPMS]. The HC of the sample is calculated by subtracting the addenda measurement from the total heat capacity measurement. The total HC is the measurement of the HC of the sample, the grease, and the sample platform. The two measurements-one
with and one without the sample on the sample platform are necessary for accuracy. In order to ensure the further accuracy of our results, we conducted the experiment several times. We note that automatic subtraction of the addenda, at each sample temperature measurement is performed. We have performed the measurement in the temperature range 295-38 K.

3 Results and Discussion

Fig. 1 shows the $\beta$-FeSi$_2$ needle-like crystal used in heat capacity experiment. The crystal is approximately 5 mm in length and with a 1 mm diameter. The mass is $1.26 \pm 0.01$ mg. Fig. 2 through Fig. 5 show the results of our HC measurements. The the results of the addenda measurement, along with the corresponding error are shown in Fig. 2. It is clear that the addenda data is smooth as it should be, without any jumps which could confuse the interpretation of the sample data. As can be clearly seen the error is negligible. The sample HC and the corresponding error are shown in Fig. 3. The error is very small compared to the value of the HC. The two anomalies are indicated by temperatures $T_A$ and $T_B$. To clarify the behaviour of these anomalies, we show in detail the anomaly at temperature $T_A$ in Fig. 4, and show the subtracted HC $\Delta C$ in Fig. 5. The approximate deviation at the temperature $T_A$ is on the order of 6.6-8.3 %. The broad deviation centered around $T_B$ has a maximum deviation of 6.25 % peak to peak, with respect to the value of HC at $T_B$.

What is the origin of the anomaly at $T_A$? The resistivity data clearly shows an anomaly at a temperature of 220 K [9], there is an inflection in the $\rho$-T curve, which is indicative of ”phase-transition” rather than a cross-over. Now our HC measurements strongly suggest the existence of a ”phase-transition”. Incidentally this clarifies the discrepancy between band-structure calculations and magneto-transport experiments mentioned previously in the introduction-since one can argue that band structure changes, with some bands having very sharp edges, as a result of the phase transition. In addition the TTE measurements also confirm this scenario-these measurements indicate that that the system undergoes from single carrier system to at least two carrier system at approximately 220 K. The anomaly which is centered around approximately 160 K, Fig. 5, lies in region $100 \leq T \leq 250$ K. This roughly coincides with Region II ($\approx 90 \leq T \leq 220$ K) in the notation of Hara et al.[9]. In this region the behaviour of resistivity $\rho$ indicates that the system behaves as a degenerate semiconductor with density of states, which is finite even at absolute zero. In addition from the Hall measurements, in this region non-linear Hall effect was observed, which is suggestive that the system behaves as a multiple carrier one. This also fits nicely with the slow broad deviation, shown here in Fig. 5 as the change of HC from the smooth background- covering the whole region between 100 K and 250 K.
4 Conclusions

In conclusion we have measured the HC of needle-like single crystals of $\beta$-FeSi$_2$ single crystal, grown by chemical vapor transport. We found two anomalies, which can be related to the ones found previously in the measurements of resistivity and TTE. Thus providing evidence and clarification of the resistivity and TTE data. Very importantly if one assumes that the ”phase transition” at $T_A$ changes the band-structure in a significant way, so that some bands develop sharp edges, then this can clarify the discrepancy between the band-structure calculations and magneto-transport measurements. Our finding is significant also in the sense that it provides an independent confirmation of the previous results using an entirely different technique.

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Figure 1: Photograph of the needle-like single crystals of $\beta$-FeSi$_2$, with approximate dimensions, length=5mm, diameter=1 mm.
Figure 2: The Addenda HC [μ J/K] and the error used for the sample.

Figure 3: The sample HC [μ J/K] and the corresponding error.
Figure 4: The main HC anomaly in more detail.

Figure 5: The subtracted data, $\Delta C$ [${\mu}$ J/K] showing the anomalies at $T_A$ and $T_B$ for the sample.