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Electrical property of single-phase HMS grown by temperature gradient solution growth method using Ga and Sn solvent

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Abstract

We have investigated the electrical property of single-phase HMS crystals grown by a temperature gradient solution growth (TGSG) method using Ga and Sn solvent. We found the clear difference of resistivity between $Mn_{11}Si_{19}$ and Mn_4Si_7, which would be caused by the difference in their electronic structure. The hole concentration of $Mn_{11}Si_{19}$ was approximately one order of magnitude higher than that of Mn_4Si_7. This experimental result supports the theoretical prediction that the Fermi level of only Mn_4Si_7 stays in the energy gap while those of the other HMSs, namely $Mn_{11}Si_{19}$, $Mn_{15}Si_{26}$, and $Mn_{27}S_{47}$, stay inside the valence band.

1. Introduction

Higher manganese silicides (HMS)s have attracted attention as interesting materials for the thermoelectric devices and infrared optical detection devices because they have a large Seebeck coefficient, high chemical stability and narrow band gap energy [1-3]. There are at least four different tetragonal phases in HMSs, including Mn_4Si_7, $Mn_{11}Si_{19}$, $Mn_{15}Si_{26}$, and $Mn_{27}Si_{47}$ [1]. Migas et al., studied electronic structures of these HMSs by the ab initio calculation and predicted that only the Fermi level of Mn_4Si_7 stays in the energy gap while those of the other HMSs, namely $Mn_{11}Si_{19}$, $Mn_{15}Si_{26}$, and $Mn_{27}S_{47}$, stay inside the valence band regardless of the presence of the similar energy gaps (0.77 – 0.78 eV) [1].

In addition, a number of experimental studies on the band gap nature and electrical property of each HMS phase have been carried out by optical and electrical measurements. Iioka et al., investigated the optical absorption of single phase $Mn_{11}Si_{19}$ and found the indirect transition type absorption with the energy of approximately 0.64 eV at 5 K [3] . Nishida and Kawasumi et al. reported the anisotropy of the electrical property [4, 5]. However, difference in electrical property of each HMS phase is still unclear because of the difficulty in obtaining single phase HMS crystal.

Recently, we have succeeded in growing single-phase $Mn_{11}Si_{19}$ and Mn_4Si_7 bulk crystal by the temperature gradient solution growth (TGSG) method using Ga and Sn solvent, respectively [3, 6]. In this paper, we investigate the electric property of single-phase $Mn_{11}Si_{19}$ and Mn_4Si_7 crystals by Hall effect measurement between 5 and 300 K.

2. Experimental procedures

Crystal growth of single-phase $Mn_{11}Si_{19}$ and Mn_4Si_7 bulk was carried out by the TGSG method using Ga and Sn solvent, respectively. The solute of Mn-Si alloy ingot was pre-synthesized by melting the certain amount of Mn (3N) and Si (10N) (Mn:Si = 1:1.7) in a purified quartz ampoule. Then, the alloy solute and Ga (6N) or Sn (5N) solvent were encapsulated in a purified quartz ampoule with a graphite template under a high vacuum ($< 5 \times 10^{-6}$ Torr) condition. Inner diameter of the template and ampoule were 15 mm and 16 mm, respectively. The thickness of the solvent, i.e. distance between the alloy ingot and the template, was fixed at 10 mm. The encapsulated growth ampoule was placed in a resistive heating vertical furnace with temperature gradient of ΔT = 40 °C/cm. Typical growth temperature and dissolution temperature were 900 ℃ and 950 ℃, respectively. Typical growth period was 1 week (168hours). After growth, the Ga and Sn solvent were removed by aqua regia.

Electrical property of the grown crystals was evaluated by the Hall effect measurement and the van der Pauw method using the Physical Properties Measurement System (PPMS, Quantum Design). The measured temperature range and applied magnetic field were 5 - 300 K and 0 - 5 T, respectively.

3. Results and discussion

Figs.1 (a) and (b) show a typical single-phase $Mn_{11}Si_{19}$ crystal grown from Ga solvent. The crystal was about 14mm in diameter and about 0.8-1.4mm in thickness. Figs. 2 (a) and (b) show a typical single-phase Mn_4Si_7 crystal grown from Sn solvent. The crystal diameter was identical with the $Mn_{11}Si_{19}$ crystal grown from Ga solvent and the thickness was about 0.3mm.

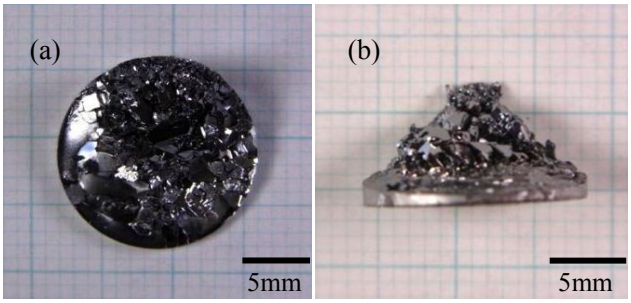

Fig.1. Top view (a) and side view (b) of typical $Mn_{11}Si_{19}$ crystal grown from Ga solvent.

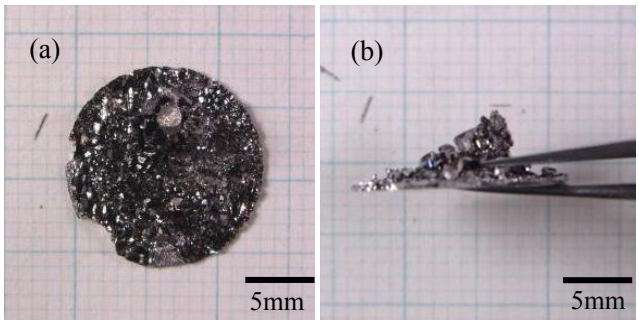

Fig.2. Top view (a) and side view (b) of typical Mn_4Si_7 crystal grown from Sn solvent.

Fig. 3 shows the temperature dependence of electrical resistivity of $Mn_{11}Si_{19}$ (sample #1 and #2) and Mn_4Si_7 (sample #3 and #4) crystals. The resistivity of #1 and #2 ($Mn_{11}Si_{19}$) was lower than that of #3 and #4 (Mn_4Si_7) in measured temperature range, although all samples showed metallic temperature dependence. The resistivity of $Mn_{11}Si_{19}$ at 300K was 1.2 x 10^{-3} and 1.1 x 10^{-3} for #1 and #2, respectively. The values are close to our previous report (0.9 - 1.1 x 10^{-3} Ωcm)[6].

Figs. 4 (a) and (b) show the temperature dependence of hole concentration and Hall mobility of $Mn_{11}Si_{19}$ and Mn_4Si_7 crystals, respectively. Interestingly, clear difference of hole concentration was found between $Mn_{11}Si_{19}$ (#1 and #2) and Mn_4Si_7 (#3 and #4). The hole concentration of $Mn_{11}Si_{19}$ was (1.6 - 3.6) x 10^{21} cm^{-3}, whereas that of Mn_4Si_7 was (1.1 - 2.7) x 10^{20} cm^{-3}. The big difference of hole concentration would be due to the difference of electronic structure between $Mn_{11}Si_{19}$ and Mn_4Si_7 as predicted by ab-initio calculation [1]. The Hall mobility was 1.6 - 2.3 cm^2/Vs for $Mn_{11}Si_{19}$ and 2.4 - 4.1 cm^2/Vs for Mn_4Si_7 at 300K. The values are close to each other. Therefor, the difference of resistivity between $Mn_{11}Si_{19}$ and Mn_4Si_7 is mainly due to the difference of hole concentration in each crystal.

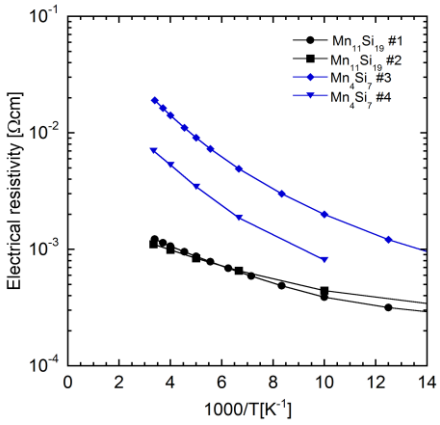

Fig.3 Temperature dependence of resistivity of single-phase $Mn_{11}Si_{19}$ and Mn_4Si_7 crystals.

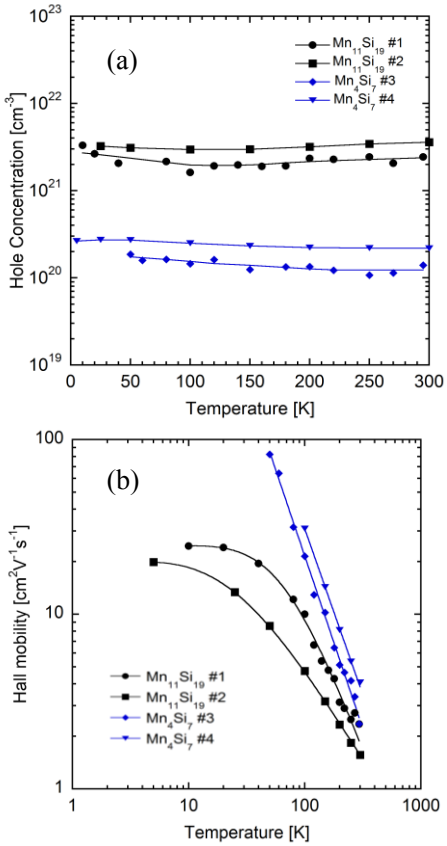

Fig.4 Temperature dependence of (a) hole concentration and (b) Hall mobility of single-phase $Mn_{11}Si_{19}$ and Mn_4Si_7 crystals.

4. Conclusion

We have studied the electrical property of single-phase Mn_4Si_7 and $Mn_{11}Si_{19}$ crystals grown by the temperature gradient solution growth (TGSG) method using Ga and Sn solvent, respectively. Clear difference of resistivity that would be caused by the difference in their electronic structure was found between $Mn_{11}Si_{19}$ and Mn_4Si_7 crystals. The hole concentration of $Mn_{11}Si_{19}$ was approximately one order of magnitude higher than that of Mn_4Si_7. The higher hole concentration in $Mn_{11}Si_{19}$ supports the theoretical results that the Fermi level of only Mn_4Si_7 stays in the energy gap while those of the other HMSs, namely $Mn_{11}Si_{19}$, $Mn_{15}Si_{26}$, and $Mn_{27}S_{47}$, stay inside the valence band.

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