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溶融塩法による $MnSi_{1.7}$ バルク結晶の成長と構造特性

Growth and structural property of $MnSi_{1.7}$ bulk crystals by molten salt method

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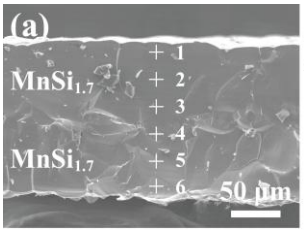
Introduction: Higher manganese silicides (HMS) with a direct band gap of about 0.7 eV, the important transition-metal silicides, are considered to be appropriate semiconducting materials for use in thermoelectric devices due to their large Seebeck coefficient, low resistivity and high oxidation resistance [1-3]. HMS has a tetragonal crystalline structure with a lattice constant of a = 0.553 nm and an unusually long c-axis up to 10 nm [4]. The unusual crystalline structure of HMS makes it difficult to grow high quality bulk crystals. Although various techniques for the growth of HMS layers have been developed, such as RDE, MBE and IBE [4], these growth techniques require an ultra-high vacuum atmosphere during the growth and difficult to grow the thick HMS layers or bulk crystals. However, it is important to develop a simple and vacuum-free technique for the growth of the HMS bulk crystals. In this study, a vacuum-free simple growth technique has been demonstrated for the growth of $MnSi_{1.7}$ bulk crystals.

Experiments: $MnSi_{1.7}$ bulk crystals were grown using MnSi substrates by the molten salt method. The salt is composed of 73.16 mol% NaCl–21.95 mol% NaF–4.89 mol% Na_2SiF_6 [5]. The salt mixture and silicon powder (21.85 mol% for the salt mixture) were placed in an SiO_2-Al_2O_3 crucible with the MnSi substrates. They were thermally treated at the temperatures between 700 °C and 900 °C for 1 to 48 h at atmosphere. After the heat treatment the salt was removed from the sample using deionized H_2O.

Results and Discussion: Figure 1 shows SEM image and EDS resuts of the $MnSi_{1.7}$ bulk crystal grown at the temperature of 900 °C for 36 h by molten salt method. The $MnSi_{1.7}$ bulk crystal with a thickness about 150 μm is formed homogeneously. The domain boundary at the center is the interface where the $MnSi_{1.7}$ domains are grown from both sides of the MnSi and meet at the center of the crystal. No voids or other defects are observed in the as-grown layers except the hole defect derived from the original MnSi substrate. The results of the EDS measurements reveal that the elemental composition is Mn/Si=1:1.7 in the whole crystal. The growth condition dependence of the thickness of $MnSi_{1.7}$ layers on the MnSi substrates is investigated. In addition, the growth mechanism of $MnSi_{1.7}$ layer will be discussed.



Atomic percent		
	Mn	Si
1	36.26	63.74
2	36.25	63.75
3	37.27	62.73
4	36.86	63.14
5	36.94	63.06
6	35.60	64.40

Fig.1 Cross-sectional SEM image and EDS results of the $MnSi_{1.7}$ bulk crystal grown at 900 °C for 36 h

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