Electric resistivity and conduction mechanism for molten Sb₂Te₃-GeTe system

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ABSTRACT

The aims of this study are to measure electric resistivity of the molten Sb₂Te₃-GeTe pseudo binary system and to investigate the compositional dependence of electric resistivity and the conduction mechanism. The samples used were Sb₂Te₃, GeSb₄Te₇, GeSb₂Te₄, Ge₂Sb₂Te₅ and GeTe. The measurements were conducted using the four-terminal method over temperature ranges between the respective melting temperatures of the samples and 1150 K during both cooling and heating cycles. Electric resistivity for all the samples decreased with increasing temperature, suggesting that the samples are liquid semiconductors. In the Sb-Te system, Sb₂Te₃ had the largest electric resistivity at a certain temperature; on the other hand, significant compositional dependence was not found in the Sb₂Te₃-GeTe system. The measurement of electro motive force suggested that the carrier of Sb₂Te₃ and Ge₂Sb₂Te₃ were hole, *i.e.*, the samples are p-type semiconductors. The compositional dependence of electric resistivity is explained from the viewpoints of enthalpy of mixing.

Keywords Sb-Te alloy, Phase Change Memory, Electric resistivity, liquid

1. INTRODUCTION

The chalcogenides in the Sb₂Te₃-GeTe pseudo binary system such as $Ge_2Sb_2Te_5$ are used as phase change materials (PCM) in phase-change random access memory(PRAM)[1]. PRAM utilizes the electric resistance contrast associated with phase change for data storage. Accordingly, the electric resistivity of PCMs is essential to optimal operation of PRAM devices. There is one report available about electric resistivity of liquid $Ge_2Sb_2Te_5[2]$, and the resistivity shows negative temperature dependence, suggesting that $Ge_2Sb_2Te_5$ is liquid semiconductor. Furthermore, to understand the conduction mechanism it is essential to determine the carrier type. The present work aims to measure electric resistivities of the Sb₂Te₃-GeTe pseudo binary system in the liquid state and to determine the carrier type of liquid Sb₂Te₃ and Ge₂Sb₂Te₅.

2. EXPERIMENTAL

Samples used in this study were Sb₂Te₃, GeSb₄Te₇, GeSb₂Te₄, Ge₂Sb₂Te₅ and GeTe: all of these compositions are in Sb₂Te₃-GeTe pseudo binary system. Reagent grade Sb₂Te₃ and GeTe powders were weighed to the desired compositions and mixed in an alumina mortar. Electric resistivities were measured using the four-terminal method[2] over temperature ranges between the respective melting temperatures of the samples and 1150 K during both cooling and heating cycles. The electromotive force of the cylindrical samples was also measured for Sb₂Te₃ and Ge₂Sb₂Te₅ by applying temperature difference of 10 - 30 K to the sample.

3. RESULTS AND DISCUSSION

Figure 1 shows the electric resistivity of solid and liquid GeSb₂Te₄: the values for liquid are measured in this study and those for solid are reported by Konstantinov et al[3]. The electric resistivity increases with increasing temperature up to about 750 K, which temperature dependence is same as that for metal. However, above 750 K, the electric resistivity decreases with increasing temperature in both solid and liquid states, which temperature dependence is same as that for semiconducting Si. Furthermore, the electric resistivity decreases drastically associated with melting. This temperature dependence of electric resistivity was also observed for other samples. Figure 2 shows measured Seebeck coefficient of Sb₂Te₃ together with reported values. The Seebeck coefficient increases with increasing temperature in the solid state and drastically decreases with melting. The Seebeck coefficient is positive. This suggests that the carrier of Sb₂Te₃ is hole, *i.e.*, the sample is p-type liquid semiconductor. Ge₂Sb₂Te₅ was also considered to be p-type semiconductor in liquid state. Figure 3 shows GeTe concentration dependence of electric resistivity for Sb₂Te₃-GeTe system at 1070 K. GeSb₂Te₄ shows the largest electric resistivity; however, the compositional dependence is not significant compared with that for Sb-Te system. To investigate the compositional dependence for electric resistivity for both systems, firstly, the pseudo gap energy(*E_a*), *i.e.*, the energy between Fermi energy and mobility edge in the valence band, was calculated for all the samples in liquid states on the basis of the following equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

where σ , σ_0 , k and T represent electric conductivity, *i.e.* the reciprocal of electric resistivity, a constant, Boltzmann's constant, and temperature. The calculated value of E_a showed correlation with electric resistivity: sample which has larger electric resistivity showed greater activation energy. The activation energy would relate to bonding energy between atoms, which can be evaluated form enthalpy of mixing. Figures 4 shows enthalpy of mixing for Sb₂Te₃-GeTe systems[6]. The enthalpy of mixing shows no significant compositional dependence, which suggests that the interaction between Sb and Ge is small in this system, and Sb and Ge atoms are mainly bonding with Te atoms. This suggests that the carriers, *i.e.*, holes in this system, move thorough Te atoms to other atoms.

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Fig. 1 Temperature dependence of electric resistivity of $SbGe_2Te_4$



Fig. 3 Electric resistivity of Sb_2Te_3 -GeTe system at 1070 K as function of GeTe concentration



Fig. 2 Temperature dependence of Seebeck coefficient of Sb_2Te_3 with reported data[4, 5]



Fig. 4 Enthalpy of mixing for Sb₂Te₃-GeTe system as a function of GeTe concentration [6]