phys. stat. sol. (b) **198**, 497 (1996)

Subject classification: 72.20; S7.13

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ZnSb and GaSb Bulk Amorphous Semiconductors: Transport Properties

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(Received June 14, 1996)

Temperature dependencies of the conductivity and thermopower of bulk amorphous semiconducting alloys $Zn_{41}Sb_{59}$ and $Ga_{100-x}Sb_x$ with $47.5 < x < 55$ were measured at 80 to 370 K and 120 to 370 K, respectively. The samples were prepared by solid state amorphization of the quenched high pressure phases occurring on heating at ambient pressure. The electrical properties of nonstoichiometric a-$Zn_{41}Sb_{59}$ are well described by the conventional Mott-Davis model. Those of both stoichiometric a-GaSb and nonstoichiometric a-$Ga_{100-x}Sb_x$ appear to be more unusual and require a modification of the model.

1. Introduction

Amorphous $Ga_{50}Sb_{50}$ and $Zn_{41}Sb_{59}$ were the first bulk amorphous semiconductors produced by a solid state reaction using spontaneous amorphization of a metastable crystalline high pressure phase [1, 2]. The amorphous samples obtained in this way were shown to contain no crystalline or nanocrystalline inclusions [3 to 5]. The purpose of the present work was to study and compare the transport properties of stoichiometric a-$Ga_{50}Sb_{50}$ and nonstoichiometric a-$Zn_{41}Sb_{59}$ and a-$Ga_{100-x}Sb_x$ with $47.5 < x < 55$.

2. Experiment

The initial ingots were prepared by alloying appropriate amounts of elements (each 99.999 wt% pure). The alloys were transformed to the high-pressure metallic phase, quenched to 100 K and unloaded at this temperature to retain this phase in a metastable state, and then heated at ambient pressure up to room temperature for amorphization. The details of the procedure are described elsewhere [3, 6]. The X-ray examination of the samples (DRON-2.0 diffractometer, CuK_α radiation) revealed no traces of crystalline phases. The dc-conductivity σ and the thermoelectric power S were measured at temperatures from 80 to 370 K and 120 to 370 K, respectively.

3. Results and Discussion

Typical temperature dependencies of σ and S for a-$Zn_{41}Sb_{59}$ are shown in Fig. 1. The $\sigma(T)$ curves correspond to an activated behaviour with an activation energy E_σ varying

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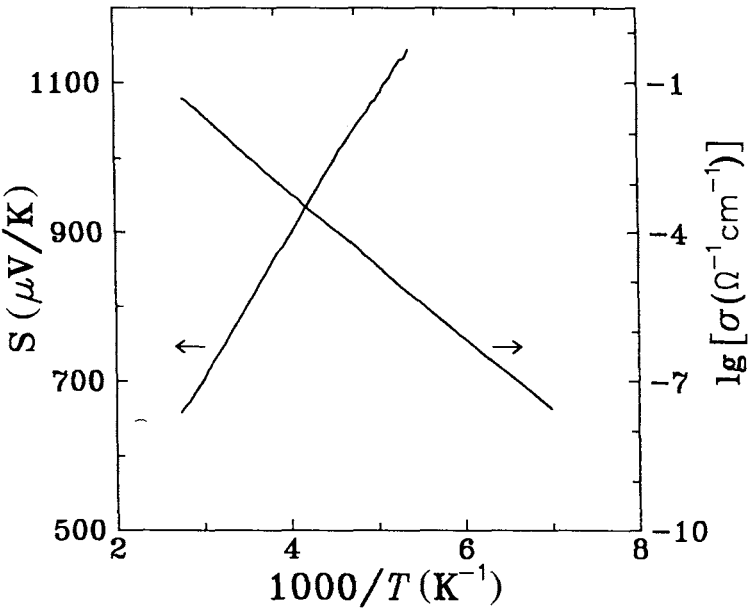

Fig. 1. Temperature dependencies of the electric conductivity σ and thermopower S for amorphous $Zn_{41}Sb_{59}$

from sample to sample in the range 0.27 to 0.30 eV. The thermopower was positive and increased approximately linearly with the reciprocal temperature: $S = (k/e) \times ([E_S/kT] + C)$ with $E_S = (0.19 \pm 0.01)$ eV and $C = 1 \pm 0.5$ (k is the Boltzmann constant, e the elementary charge).

The $\sigma(T)$ and $S(T)$ data for a-$Ga_{100-x}Sb_x$ with $x = 47.5$, 50, 52.5, and 55 are presented in Fig. 2 and 3. As one can see from Fig. 2, at $T > 180$ K all samples display activation type conductivities with $E_\sigma = 0.20$, 0.26, 0.28, and 0.30 eV, respectively. At lower T, the slope of $\lg(\sigma)$ versus T^{-1} decreases gradually.

The S values of the amorphous Ga–Sb alloys were also positive. However, they varied with respect to T^{-1} approximately linearly only at high temperatures and decreased steeply towards zero for $T < 150$ to 200 K (except $x = 47.5$). The temperature range of the activation behaviour of $\sigma(T)$ corresponds roughly to the region of the slow linear changes in $S(1/T)$. Within this temperature range, the slope of the $S(1/T)$ dependence was positive for $x = 55$ and negative for $x \leq 52.5$.

The electrical properties of a-$Zn_{41}Sb_{59}$ are characterized by an activation type conduction with E_σ close to one half of the band gap of the crystalline semiconductor ZnSb. The thermopower is positive, increaseses nearly linearly with T^{-1}, and we have $E_S < E_\sigma$. These results are typical for many amorphous semiconductors [7 to 9] and are well described by the conventional Mott-Davis model [7].

According to this model, the Fermi level E_F is pinned close to the middle of the mobility gap, where a peak in the density of states for partly filled localized states is situated. A positive sign and a large value of S suggest that the conductivity is due to holes excited to the states near the mobility edge E_V of the valence band. The relationship $E_\sigma > E_S$ indicates that the conduction is dominated by thermally activated hopping of

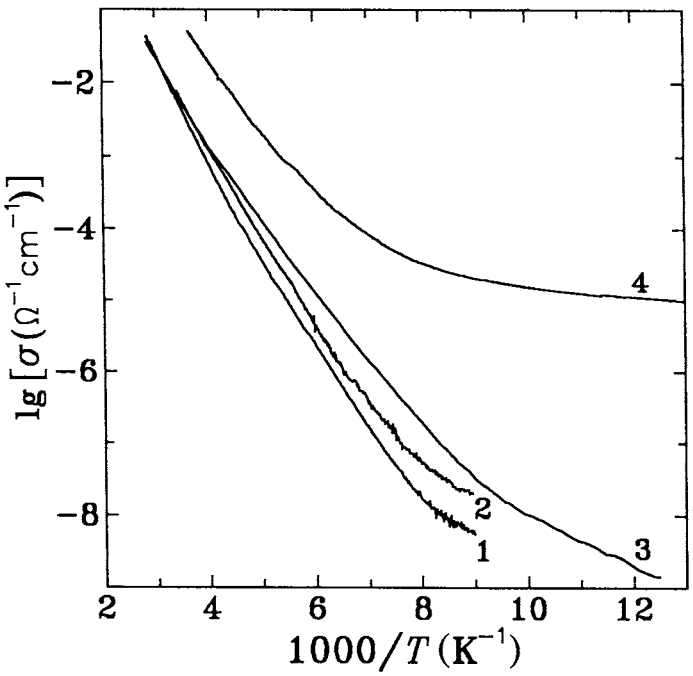

Fig. 2. Temperature dependences of σ for amorphous $Ga_{100-x}Sb_x$ with $x = (1)$ 55, (2) 52.5, (3) 50, and (4) 47.5

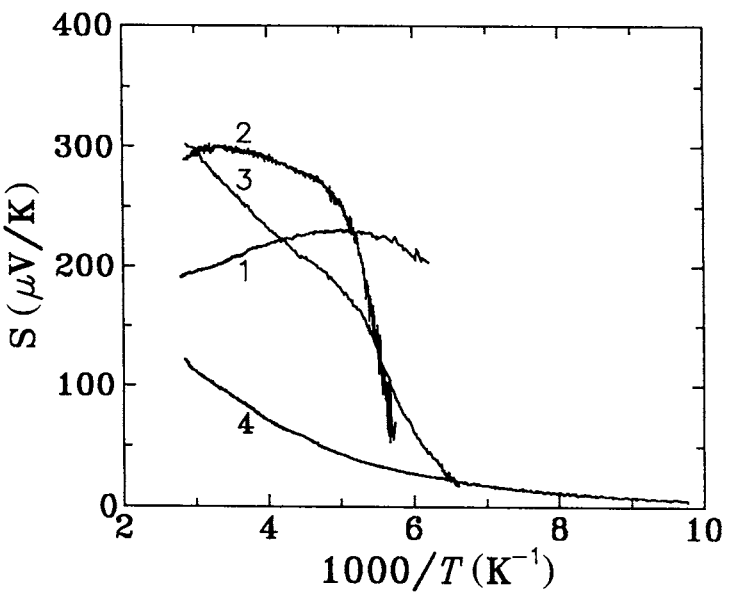

Fig. 3. Temperature dependences of S for amorphous $Ga_{100-x}Sb_x$ with $x = (1)$ 55, (2) 52.5, (3) 50, and (4) 47.5

the carries between localized states of the valence band tail, with the corresponding edge E_A. In this case $E_S = E_F - E_A$ and $E_\sigma \approx E_S + W$, where W is the activation energy of the hole hopping mobility. For the a-$Zn_{41}Sb_{59}$ we therefore have $E_F - E_A \approx 0.19$ eV and $W \approx 0.1$ eV.

In contrast to non-stoichiometric a-$Zn_{41}Sb_{59}$, the transport properties of stoichiometric and nearly stoichiometric a-Ga–Sb cannot be explained on the basis of a single conductivity mechanism. Besides, since the properties of a-$Ga_{100-x}Sb_x$ alloys change gradually with x varying over the whole concentration range (Fig. 2 and 3), one needs a model attributing the concentration dependence of these properties to a gradual variation of certain model parameters. In particular, it is essential to explain the values and signs of the high temperature $dS/d\,(1/T)$ for different x.

Most unusual are the $S(1/T)$ dependencies of the alloys with $x \leq 52.5$, characterized by negative values of $dS/d\,(1/T)$ remaining nearly constant over wide temperature ranges.

The large values of $S > k/e$ (nondegenerate case) combined with $dS/d\,(1/T) < 0$, observed in a-$Ga_{100-x}Sb_x$ samples with $x \leq 52.5$ at higher temperatures are usually described by a competition of several types of conductivity mechanisms coexisting within the same temperature interval, because hopping conductivity near the Fermi-level, the only mechanism resulting in $dS/d\,(1/T) < 0$, cannot give large values for S [7]. Within the framework of the conventional models, however, even a combination of two or more conduction mechanisms cannot yield a constant value of $dS/d\,(1/T)$ over a wide temperature interval and should result in an $S(1/T)$ dependence with a maximum. One can get a rather simple and more natural explanation of the effects observed in a-Ga–Sb if one allows for $E_A > E_F$ in contrast to the usual models with $E_A < E_F$ for the p-type amorphous materials.

Using the standard semi-quantitative approach [7], one may suppose that the density of states in the band tail is $N(E) \propto (E_A - E)^n$. At sufficiently high temperatures, when σ is mainly due to the band tail states, most holes in the tail are located near the maximum of $N(E)\exp([E - E_F]/kT)$ at $E_m = E_A - nkT$. With $E_A < E_F$ this is true even at low temperatures, but with $E_A > E_F$ it is valid only at $kT < E_F - E_m$, that is at $kT > (E_A - E_F)/(n-1)$. Under these conditions $\sigma \propto T^n \exp([E_A - E_F + W]/kT)$ and $S \approx (E_F - E_m)/eT = k/e([E_F - E_A]/kT + n) \approx k/e([E_F^0 - E_A^0]/kT + C)$, where E_F^0 and E_A^0 correspond to $T = 0$ K. As a rule, $n - 2 < C < n - 1$ due to a decrease in the band gap with increasing temperature. The given formulae are common except that the difference $E_F - E_A$ can have any sign. This allows for a linear variation of $S(1/T)$ with $dS/d\,(1/T)$ of either sign.

The model parameters which determine $\sigma(T)$ and $S(T)$ are $E_F^0 - E_A^0$, C and W. For the amorphous a-$Ga_{100-x}Sb_x$ alloys with $x = 47.5$, 50, 52.5 and 55 these are $E_F^0 - E_A^0 \approx -0.04$, -0.04, -0.02 and $+0.02$ eV; $C \approx 2.6$, 4.7, 4.2, and 1.5; $W \approx 0.24$, 0.30, 0.30, and 0.28 eV, respectively.

The mechanism outlined above governs the transport properties of a-Ga–Sb at temperatures higher than 150 to 200 K. With decreasing temperature, the conductivity resulting from the states near the Fermi level becomes dominating which leads to a steep decrease in S.

In conclusion, the measured electric properties of a-$Zn_{41}Sb_{59}$ show that this alloy is a classical amorphous semiconductor well described by the regular Mott-Davis model throughout the temperature interval of the present study. The dominant mechanism for

the conductivity σ and thermopower S is thereby a thermally activated hopping of holes excited into the tail of the valence band. The a-Ga–Sb alloys show more complex transport properties, which could be explained in the framework of a slightly modified Mott-Davis model with the assumption that the Fermi level might be positioned inside the band tail.

Acknowledgements The present work was supported by Grant No. 96-02-18545 from the Russian Foundation for Fundamental Research. One of the authors (O.I.B.) thanks the Organizing Committee of HPSP-VII and the International Science Foundation for financial support to attend the Conference.

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