Electrical properties of bulk amorphous semiconductor $(GaSb)_{38}Ge_{24}$

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Abstract

Temperature dependences of the dc conductivity and thermopower of a $(GaSb)_{38}Ge_{24}$ homogeneous bulk amorphous alloy are investigated at 110–425 K and at 180–400 K, respectively. The samples were prepared by spontaneous solid-state amorphization of a quenched crystalline high-pressure phase heated from 77 to 430 K at ambient pressure. In contrast to the parent amorphous GaSb compound exhibiting an unusual combination of electrical properties, amorphous $(GaSb)_{38}Ge_{24}$ is found to be a typical p-type semiconductor well described by the conventional Mott–Davis model.
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1. Introduction

A number of crystalline high-pressure phases transform, at least partly, to a metastable amorphous state when the pressure is released [1,2]. The most effective means to produce bulk homogeneous amorphous samples free of crystalline inclusions is to retain such a high-pressure phase at ambient pressure by cooling it to liquid nitrogen temperature prior to releasing the pressure and then to heat this phase over the temperature interval of its spontaneous amorphization at ambient pressure [3–6]. Today, the electrical properties have been studied for three amorphous (a-) semiconductors prepared in this way: a-$Zn_{41}Sb_{59}$ [7], a-$Al_{32}Ge_{68}$ [8] and a-GaSb [9].

The a-$Zn_{41}Sb_{59}$ alloy was found [7] to be a typical amorphous semiconductor with an activated behavior of the electrical conductivity σ and a linear increase in the thermopower S with increasing $1/T$. By contrast, the a-$Al_{32}Ge_{68}$ [8] and a-GaSb [9] alloys showed combi-

nations of $\sigma(T)$ and $S(T)$ dependences never observed in amorphous semiconductors. The unusual electrical properties of these alloys were described semi-quantitatively [8,9] in terms of a modified Mott–Davis model assuming that the Fermi level lies inside the valence band tail.

The composition of the a-$Zn_{41}Sb_{59}$ and a-$Al_{32}Ge_{68}$ alloy cannot be varied since it is limited by the narrow homogeneity range of the corresponding high-pressure phase. The metallic high-pressure phase of GaSb forms a continuous solid solution with the metallic high-pressure phase of Ge, and samples of this crystalline GaSb–Ge solution transform into amorphous semiconductor state when the pressure is released [10,11]. As the first step to studying the effect of varying composition in the GaSb–Ge system, this paper reports on the electrical properties of amorphous $(GaSb)_{38}Ge_{24}$ semiconductor.

Stable and metastable transformations in the $(GaSb)_{38}$-Ge_{24} alloy were earlier investigated in a wide pressure and temperature range and a procedure to produce homogeneous amorphous samples was worked out [12]. The structure of bulk amorphous samples prepared by this procedure was studied by neutron diffraction and

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analysed using reverse Monte Carlo simulations [6]. The samples were shown to be homogenous amorphous compounds free of any crystalline phases. The average nearest-neighbour co-ordination number equals 4.25 that exceeds 4 and therefore points to a noticeable distortion of the tetrahedral arrangement in the alloy. The Ge atoms randomly substitute the Ga and Sb atoms in the network characteristic of amorphous GaSb semiconductor investigated in [5]. The arrangement of the Ga and Sb atoms in a-$(GaSb)_{38}Ge_{24}$ demonstrate approximately the same degree of disorder as in a-GaSb, and about 30% nearest neighbours are the atoms of the same kind (Ga–Ga or Sb–Sb pairs).

2. Experimental

To prepare amorphous $(GaSb)_{38}Ge_{24}$ samples in the present work, we used the same starting alloy and the same procedure as in Refs. [6,12].

The ingot of the $(GaSb)_{38}Ge_{24}$ alloy was melted from 99.999% Ga, Sb and Ge, crushed into powder in an agate mortar and pressed into pellets 8 mm in diameter and 5 mm thick. Each pellet was placed in a Teflon container and exposed to 7.7 ± 0.3 GPa and 250 ± 7 °C for 24 h in a toroid-type high-pressure chamber. The chamber was then cooled to 100 K, the pressure was lowered to atmospheric, the pellet was taken out of the chamber and X-rayed at 100 K to check that it consisted of the high-pressure metallic phase only. The recovered pellet was brought to the amorphous state by heating to 150 °C = 423 K at a rate of 20 °C min^{-1}, then cooled to room temperature at 200 °C min^{-1} and X-rayed to check for the absence of crystalline inclusions.

Three samples in the form of bars $1 \times 1 \times 5$ mm^3 were cut out of different amorphous pellets with an abrasive wire saw. Copper electrodes were stuck to the samples with silver paste. The dc conductivity, σ, and the thermoelectric power, S, were measured at temperatures from 110 to 425 K and from 180 to 400 K, respectively.

3. Results

Typical temperature dependences of S and σ for a-$(GaSb)_{38}Ge_{24}$ are presented in Figs. 1 and 2. The dependences showed no hysteresis in the repeated cycles of heating and cooling of the samples. One of the samples was additionally exposed for 30 min to a temperature as high as 473 K, and its electrical properties did not change after this treatment either. Thus, the measured properties of a-$(GaSb)_{38}Ge_{24}$ were not changing in the course of experiment due to any relaxation processes that might occur in the metastable samples.

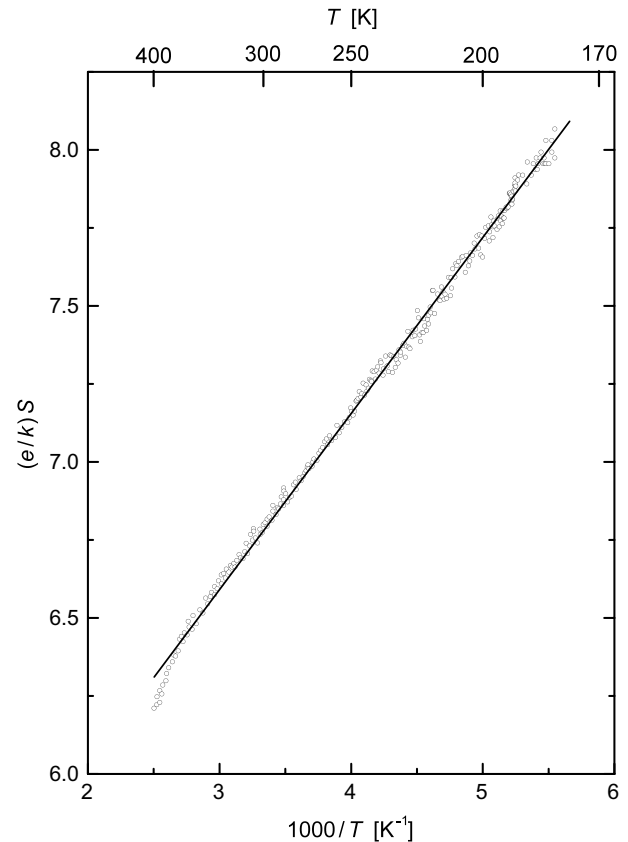As seen from Fig. 1, the thermopower of a-$(GaSb)_{38}Ge_{24}$ is positive. This points to the p-type of

Fig. 1. A representative dependence of the thermopower S vs. reciprocal temperature for $(GaSb)_{38}Ge_{24}$ amorphous semiconductor (open circles) and its linear fit (solid line). e is the elementary charge, k is the Boltzmann constant.

the conductivity, which is characteristic of most amorphous semiconductors. The thermopower increases approximately linearly with increasing reciprocal temperature. A linear dependence of $S(T^{-1})$ in a wide temperature range is typical of many amorphous semiconductors and it is usually presented in the form:

$$Se/k = E_S/kT + C, \qquad (1)$$

where the values of E_S and C are temperature-independent. In our case, the energy $E_S = 0.05 \pm 0.005$ eV and the dimensionless constant $C = 5 \pm 0.2$.

An inset to Fig. 2 shows the $\lg(\sigma)$ vs. T^{-1} dependence for a-$(GaSb)_{38}Ge_{24}$. One can see that the conductivity is of an approximately activated character. The activation energy $E_{act}(T) = -d(\ln\sigma)/d(1/kT)$ varies from 0.16 to 0.37 eV with the temperature increasing from 110 to 425 K. If the temperature dependence of σ is written in the standard form $\sigma(T) = A \cdot \exp(-E_A/kT)$ with E_A constant, the pre-exponential factor A therefore increases with T. In the case of a-semiconductors, $A(T)$ at high temperatures is usually approximated as BT^n [13,14]:

$$\sigma(T) = BT^n \cdot \exp(-E_A/kT). \qquad (2)$$

Varying n in the experimental $\lg(\sigma/T^n)$ vs. T^{-1} dependences gives $n \approx 4$, $E_A \approx 0.2$ eV and $B \approx 10^{-9}$
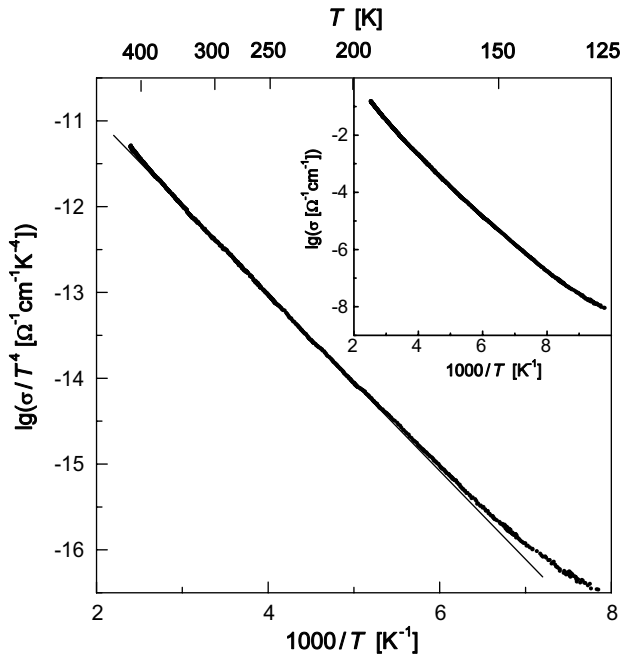
Fig. 2. A representative temperature dependence of the dc conductivity σ for a-(GaSb)$_{38}$Ge$_{24}$ in the co-ordinates lg(σ) vs. T^{-1} (inset) and lg(σ/T^4) vs. T^{-1} (main figure). The solid line is the linear fit to the experimental dependence at $180 \leqslant T \leqslant 400$ K.

Ω^{-1} cm^{-1} K^{-4} as the parameters of the best linear fit in the temperature interval 180–400 K where S is measured. With $n = 4$, our samples showed the scatter in the value of E_A from 0.18 to 0.22 eV and in the value of B from 0.7×10^{-9} to 1.4×10^{-9} Ω^{-1} cm^{-1} K^{-4}.

The difference between the energies E_A and E_S characterising, respectively, the temperature dependence of conductivity and thermopower is about $0.2 - 0.05 = 0.15$ eV.

4. Discussion

In a rather large temperature interval of 180–400 K, amorphous (GaSb)$_{38}$Ge$_{24}$ shows electrical properties typical of classic amorphous semiconductors, which are characterized by a nearly activation type of conductivity, by a nearly linear increase in the thermopower with reciprocal temperature and by the difference $E_A - E_S$ on the order of 0.1 eV [13,14].

According to the conventional Mott–Davis model [13], the Fermi level E_F in amorphous semiconductors is pinned in the mobility gap at a relatively narrow peak in the density of states $N(E)$ for charge carriers. The peak is positioned near the middle of the gap and originates from defects in the random network, such as dangling bonds, vacancies, etc. In the framework of this model, the electrical properties of amorphous semiconductors at moderate temperatures are mainly determined by hopping conductivity of carriers thermally

excited into the band tails. The tails originate from the absence of the long-range order in amorphous substances and are assumed not to overlap with the Fermi-peak.

The magnitude of S is determined by the average distance δE_{avr} between E_F and the conducting levels [13,15]

$$Se/k = \delta E_{avr}/kT. \tag{3}$$

The distance δE_{avr} for a-(GaSb)$_{38}$Ge$_{24}$ varies from 0.12 eV at 180 K to 0.22 eV at 400 K and it is 6 to 8 times greater than kT. Such magnitudes of δE_{avr} are characteristic of conductivity in the band tail states. The conductivity is non-degenerate and charge carriers obey Boltzmann's statistics.

The basic parameter of the Mott–Davis model is

$$\Delta E = E_F - E_a, \tag{4}$$

where E_a is the tail edge energy. In the p-type semiconductors, this is the valence band tail and therefore $\Delta E > 0$. The density of states in the valence band tail is usually approximated as $N(E) \propto (E_a - E)^n$ with $n > 0$ [13,14] that leads to conductivity of an almost activated type

$$\sigma \propto T^n \exp[-(\Delta E + W)/kT], \tag{5}$$

where W is the average activation energy for hopping mobility in the band tail. In the same approximation [13,14]

$$Se/k \approx \Delta E/kT + n + 1. \tag{6}$$

The theory therefore gives a large value of thermopower ($Se/k > 1$) increasing linearly with reciprocal temperature.

As seen from Fig. 1, the $S(T^{-1})$ dependence of (GaSb)$_{38}$Ge$_{24}$ is nearly linear in the studied temperature interval from 180 to 400 K. A comparison of the parameters of fitting Eq. (1) to the experimental $S(T^{-1})$ dependence with the parameters of Eq. (5) yields $\Delta E = E_S = 0.05$ eV and $n = C - 1 = 4.0 \pm 0.2$. A comparison of Eq. (2), that describes the conductivity of (GaSb)$_{38}$Ge$_{24}$ at the same temperatures, with the parameters of Eq. (4) gives $\Delta E + W = E_A = 0.20 \pm 0.02$ and $n \approx 4$. Similar values of $n \approx 4$ resulting from the measurement of two different properties, thermopower and conductivity, evidence that the electrical properties of (GaSb)$_{38}$Ge$_{24}$ at temperatures from 180 to 400 K are determined for the most part by hopping conductivity of holes thermally excited into the tail of the valence band. The average activation energy for hopping mobility is $W = E_A - E_S \approx 0.15$ eV.

At temperatures lower than 150 K, the lg(σ/T^4) vs. T^{-1} dependence for (GaSb)$_{38}$Ge$_{24}$ noticeably deviates from the straight line towards higher values of conductivity (Fig. 2). The deviation is likely to be due to the growing contribution from hopping conduction in the localized states near the Fermi energy that usually dom-

inates in amorphous semiconductors at low temperatures [13,14].

The electrical properties of amorphous GaSb–Ge alloys containing up to 80 mol% Ge were earlier studied in [10]. The results of that work significantly differ from ours, presumably, due to the inhomogeneity of samples prepared in a different way. The samples in [10] were heated to 1100 °C or to 400 °C at a pressure of 9 GPa and then rapidly cooled and decompressed at room temperature. The samples heated under pressure to 1100 °C were always multi-phase, showed a metallic type of conductivity and had a considerable fraction of unidentified superconducting phases. The samples heated to 400 °C were more homogeneous, demonstrated a semiconductor behavior, and those with $\geqslant 23$ mol% Ge contained no crystalline inclusions. However, the degree of homogeneity of the samples remains questionable because the point (400 °C, 9 GPa) chosen in [10] for thermo-baric treatment was close to the T–P range of melting of the GaSb–Ge high-pressure phase [12]. This phase being a multi-component solid solution, its melting had to occur within a finite temperature and pressure interval according to the phase rule, and the samples in [10] therefore could be quenched from this very interval and inherit the inhomogeneous state.

5. Conclusions

The measured temperature dependences of thermopower S and electrical conductivity σ of bulk amorphous $(GaSb)_{38}Ge_{24}$ can be interpreted in the framework of a conventional model often used for amorphous semiconductors [13]. Throughout the temperature interval 180–400 K of the thermopower measurement, the conduction of a-$(GaSb)_{38}Ge_{24}$ is dominated by thermally activated hopping of holes exited into the tail of the valance band. In this temperature range, the conductivity is well described by the equation $\sigma = BT^n \exp[-(\Delta E + W)kT]$ and the thermopower by the equation $Se/k = \Delta E/kT + n + 1$, where $B \approx 10^{-9}$ Ω^{-1} cm^{-1} K^{-4} and $n \approx 4$. The value of $\Delta E \approx 0.05$ eV is the difference between the Fermi energy and the tail edge energy at $T = 0$ K and $W \approx 0.15$ eV is the activation energy of hopping mobility in the valence band tail.

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