Non-stoichiometry in SnTe thin films and temperature instabilities of thermoelectric properties

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Abstract

The temperature dependences of the Seebeck coefficient and the electrical conductivity for $(0\,0\,1)$KCl/SnTe monocrystalline thin films with thicknesses $d = 20$–600 nm were obtained in the range of 80–300 K. In contrast with SnTe bulk crystals, these dependences exhibited anomalies (plateaus, steps, bends). It is suggested that as temperature increases, the system passes through a number of intermediate states of quantum origin and/or corresponding to different distributions of non-stoichiometric defects (cation vacancies) over the crystal lattice. The observed effect is attributed to a high concentration of non-stoichiometric defects, which leads to the defect interaction stimulating their ordering, to loosening of the crystal lattice and to an increase in the diffusion rate. It is suggested that the observed temperature instabilities of properties are typical for other phases with high concentrations of non-stoichiometric defects.

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1. Introduction

IV–VI semiconductor compounds are widely used for thermoelectric and optoelectronic applications [1]. Recently, interest in these compounds has been stimulated by the observation of a high thermoelectric figure of merit in IV–VI superlattices, which was previously predicted theoretically [2]. The possibility of practical applications of these materials is determined, to a great extent, by the character of the temperature dependences of their electrical and thermal parameters. That is why the determination of the temperature ranges of instabilities of crystal lattice and/or electron subsystem caused

by phase transitions and relaxation processes is very important both from scientific and practical points of view.

SnTe is a semiconductor compound with a wide ($\sim 1\%$) one-sided homogeneity region and a high concentration of nonstoichiometric defects (10^{20}–10^{21} cm^{-3}) [1,3]. It is known [4] that SnTe undergoes a ferroelectric phase transition (PT) at $T_C \sim 100$ K. It was shown that an increase in the hole concentration p leads to a decrease in T_C and at $p > (7$–$8) \times 10^{20}$ cm^{-3}, the phase transition is not observed [5,6]. There are a limited number of experimental works [7–10], reporting the possibility of the existence of other phase transitions in bulk SnTe. In [7,11], temperature anomalies of the electrical resistivity ρ and the Hall coefficient R_H were revealed in the ranges of 135–150 and 200–215 K in monocrystalline SnTe thin films with $p = (3.5$–$4.5) \times 10^{20}$ cm^{-3}. These anomalies were attributed to

phase transitions connected with cation vacancy redistribution over the crystal lattice under changing temperature. In [12], the facts were reported proving proclivity of IV–VI compounds and IV–VI-based solid solutions for the manifestation of different temperature anomalies of properties, possibly of quantum nature. In [13,14], series of temperature anomalies of the electrical resistivity in island-like films and heterostructures based on IV–VI compounds were observed. The authors also suggested the possibility of quantum origin of these anomalies. In [15], in the temperature dependences of the Seebeck coefficient and the electrical conductivity of polycrystalline SnTe films with a high concentration of charge carriers ($p \sim 10^{21}$ cm^{-3}), prepared by thermal evaporation of bulk SnTe and subsequent deposition on glass substrates at room temperature, steps and bends were detected. The anomalies followed one another with a certain periodicity and, thus, proved the system's passing a number of intermediate states with increasing temperature. The question arises whether the temperature anomalies are connected with a polycrystalline structure of the films and the existence of regions (grains, microdomains) with slightly different compositions and different types of ordering. If it were the case, then in monocrystalline films these anomalies would not be observed.

The goal of the present work is to study the temperature dependences of the Seebeck coefficient S and the electrical conductivity σ of monocrystalline SnTe thin films with various thicknesses.

2. Experimental

Monocrystalline thin films of SnTe with thicknesses of $d = 20$–600 nm were prepared by the thermal evaporation of stoichiometric SnTe bulk crystals in vacuum 10^{-6} Pa and subsequent deposition onto (0 0 1) KCl surfaces at (570 ± 10) K. The film thickness was controlled using a calibrated quartz resonator. The Hall coefficient R_{H} and σ were measured using a conventional dc method in a magnetic field of 0.8 T in the temperature range of 80–300 K. The measurements were carried out on the specially prepared double-Hall cross-shaped samples. Ohmic contacts were made by soldering In to the film surface. The effective hole concentration p was calculated assuming the Hall factor to be 1. S was determined with respect to copper electrodes. All the samples were of p-type.

3. Results

In Fig. 1a, the temperature dependences $S(T)$ for the SnTe monocrystalline thin films with different thicknesses ($d = 275$ and 551 nm) and with $p \approx 4$–
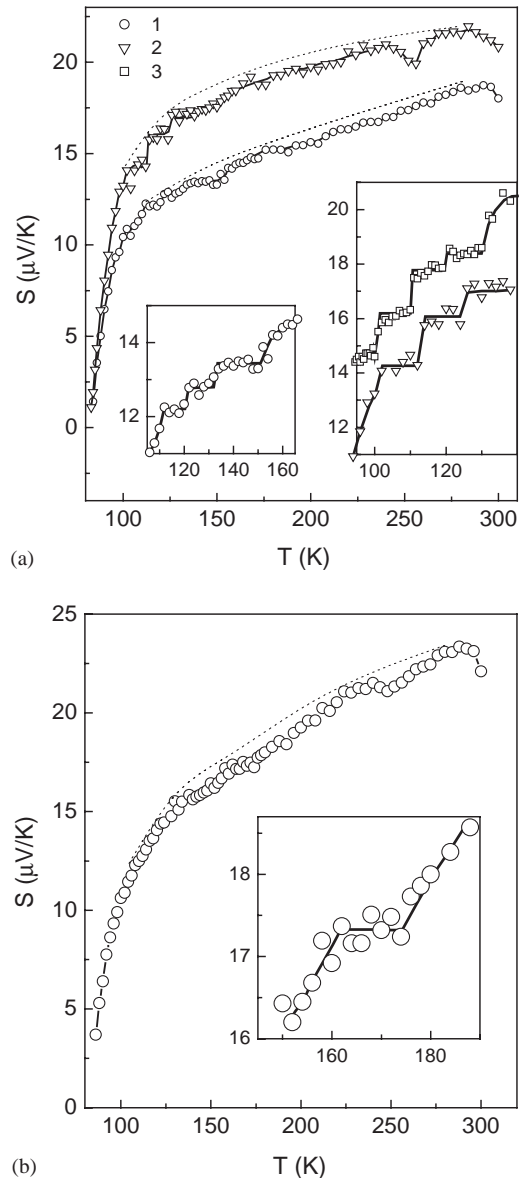

Fig. 1. The temperature dependences of the Seebeck coefficient in the monocrystalline and polycrystalline SnTe thin films. (a) 1 ($d = 551$ nm) and 2 ($d = 275$ nm) — monocrystalline films; 3 ($d = 270$ nm) — polycrystalline film [15]. (b) $d = 79$ nm — monocrystalline thin film.

5×10^{20} cm^{-3} are given. In the insert of the figure, for comparison the temperature dependence (in the range of 95–130 K) for the polycrystalline film with $d = 270$ nm and $p = 3 \times 10^{21}$ cm^{-3}, obtained in [15], is shown. In Fig. 1b, the $S(T)$ dependence for a thinner monocrystalline SnTe film with $d = 79$ nm and $p = 2.3 \times 10^{21}$ cm^{-3} is presented.

It is seen that the $S(T)$ dependences for all thin films exhibit non-monotonic behavior: the series of peculia-

rities in the form of steps and plateaus are observed. There is a certain, although not very strict, periodicity in the location of the detected anomalies on the temperature scale: in the temperature range of ≈ 80–$150\,K$, the distance between steps is equal to $\Delta T \cong 10\,K$, which corresponds to the change in thermal energy $\Delta\varepsilon \cong 0.001\,eV$. Let us point out a striking similarity of the $S(T)$ dependences in the range of 95–130 K for mono- and polycrystalline films with approximately the same thicknesses ($d = 270$–$275\,nm$), but with different hole concentrations ($p = 4 \times 10^{20}\,cm^{-3}$ and $p = 3 \times 10^{21}\,cm^{-3}$, respectively). The temperatures of some anomalies coincided with those of the phase transitions that we had observed in the SnTe thin films in the ranges of 135–150 and 200–215 K earlier [7,11]. Besides, in the studied monocrystalline films with thicknesses $d = 79$ and $275\,nm$, a distinct phase transition was detected at $\sim 250\,K$ (Fig. 1 a and b).

In Fig. 2a, the temperature dependence of the electrical conductivity $\sigma(T)$ is presented for the monocrystalline thin film with $d = 66\,nm$ and $p_{300} = 1.25 \times 10^{21}\,cm^{-3}$. Similarly to the polycrystalline thin film with $d = 270\,nm$ and $p = 3 \times 10^{21}\,cm^{-3}$ (Fig. 2b [15]), these dependences exhibit a pronounced step-like character. From the results obtained here, it follows that the character of the manifestation of anomalies and the temperature intervals between them slightly differ from film to film. It was established that anomalies of σ manifest themselves most distinctly in films with a high hole concentration ($p = 7 \times 10^{20}$–$10^{21}\,cm^{-3}$). The $\sigma(T)$ curve for bulk SnTe with a high concentration of charge carriers ($p = 8 \times 10^{20}\,cm^{-3}$), in which no anomalies are observed, is presented in Fig. 2b.

Note that when studying nuclear magnetic resonance, the authors of [10] detected "steps" in the temperature dependences of resonant fields of ^{119}Sn nuclei at $T_n = 376/n$ ($n = 1$–6). In the temperature interval, which was under consideration in this work, it corresponds to 188, 125, and 94 K, i.e. only to the temperatures, at which phase transitions in SnTe presumably connected with the redistribution of cation vacancies over the crystal lattice under changing temperature [7,11] were observed. The total number of the registered temperature anomalies was significantly greater.

It follows from the obtained data that the existence of temperature anomalies of the thermoelectric properties is typical not only for polycrystalline SnTe films but also for monocrystalline ones.

4. Discussion

The presence of multiple distinct anomalies in the $S(T)$ and $\sigma(T)$ dependences shows that under heating, the system (film) passes through a number of intermediate states. The existence of these states can be
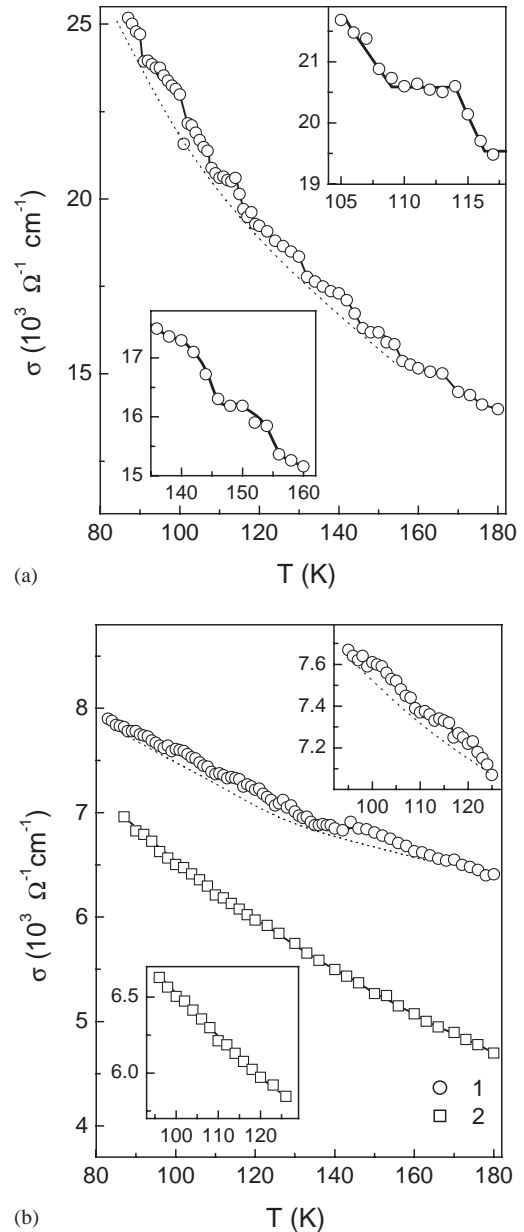

Fig. 2. The temperature dependences of the electrical conductivity in the monocrystalline (a) and polycrystalline (b) SnTe thin films and SnTe bulk crystal. (a) $d = 66\,nm$; (b) 1 — $d = 270\,nm$ (polycrystalline film); 2 — bulk SnTe (polycrystal).

caused by at least three reasons: structural reconstruction of the crystal lattice taking place with increasing temperature, relaxation processes having an oscillatory character, and the system's passing through some quantum states. Let us briefly discuss each of these possible reasons.

It is well known at present that in the case of heavily nonstoichiometric phases, broad homogeneity regions

often split into a number of ordered phases with narrower homogeneity regions. Due to a considerable contribution of the ionic component in the chemical bond in IV–VI compounds and electrical activity of nonstoichiometric defects [1], an ordered arrangement of these defects is stimulated by a noticeable energy gain.

It can be suggested that a high concentration of the nonstoichiometric defects (mainly cation vacancies) leads to loosening of the crystal lattice, an increase in the diffusion rate and facilitating of defect movement. As a result, with increasing temperature, more and more defects become involved in processes of cooperative interaction and movement. It is possible that the thin film passes through a number of subsequent, intermediate states, corresponding to different configurations of defects with the formation of configurations corresponding to the free energy minimum at a given temperature. In other words, the temperature anomalies of the thermoelectric properties can be attributed to phase transitions caused by the redistribution of native defects (nonstoichiometric vacancies) with changing temperature. Since diffusion takes place faster in a thin film due to its small volume, it is not surprising that in bulk crystals these phase transitions are not observed (Fig. 2b).

In a polycrystalline film, a microdomain structure can be realized, when a crystal contains regions of various compositions with different types of ordering. The probabilities of the formation of commensurable superstructures with periods multiple of the period of the initial lattice and the emergence of a set of discrete structural states are quite high. This can be a cause underlying a large number of temperature anomalies observed in IV–VI compounds and solid solutions on their basis [12]. However, the existence of temperature anomalies in a monocrystalline film shows that it is not polycrystalline structure of a film that causes non-monotonic behavior of the $S(T)$ and $\sigma(T)$ dependences.

The periodicity in the location of anomalies allows us to suggest that the observed phenomenon can be described using the model of quantum states proposed in [16]. According to this model, there is a set of discrete quantum states, through which the system under heating passes successively, if necessary conditions are held. The existence of such states is treated by the authors as a universal physical phenomenon, although the nature of these states is still unclear. If such a universal subsystem of quantum states actually exists, the probability of detecting these states depends on a number of factors determined by the object and conditions of observation.

From our point of view, it is possible to attribute the step-like character of the temperature dependences of σ and S to quantum character of the crystal phonon spectra. The quantization of the phonon spectra manifests itself in low-dimensional structures (thin films) under decrease in system size (quantum size effect).

It can be assumed that a high concentration of cation vacancies caused by a significant deviation from stoichiometry in SnTe, which leads to loosening of the crystal lattice, lowering of the diffusion activation energy, and an increase in the rate of diffusion, stimulates both structural reconstruction of the lattice and the manifestation of the indicated quantum states [16]. Recently, interest in objects, in which there are two weakly linked atom subsystems (superionic conductors, intercalated crystals, atomic monolayers on crystal surfaces), has grown. It is weak interaction between sublattices that leads to a variety of phase transitions observed in such structures, the possibility of the formation of long-period commensurable and incommensurable structures, a high diffusion mobility of atoms in one of the sublattices, and so on.

One should not rule out that in thin film plunged in liquid nitrogen, the approaching of equilibrium can have an oscillatory character. This oscillatory character of relaxation processes can be stimulated by a high concentration of the hole gas, in which the excitation of plasma oscillations is possible.

One can suggest that the observed temperature instabilities of properties are also typical for other phases with high concentrations of non-stoichiometric defects. To establish the origins of the detected anomalies of the temperature dependences of the thermoelectric properties and mechanisms responsible for phase transitions, additional studies are required.

5. Conclusions

The non-monotonic step-like character of the temperature dependences of the Seebeck coefficient S and the electrical conductivity σ in the SnTe monocrystalline thin films with hole concentration $p \sim (0.3–1) \times 10^{21} \, cm^{-3}$ in the range of 80–300 K was established. Earlier similar anomalies were observed only in polycrystalline films. From the results obtained in this work, it follows that the existence of anomalies is not connected with polycrystalline structure of films but caused by other, more general reasons.

One of the possible reasons for the appearance of these temperature anomalies of the thermoelectric properties is defect redistribution under heating, which results in the formation of a configuration more stable at a given temperature. The transition from one configuration to another is facilitated by an increase in the rate of diffusion processes due to a high concentration of cation vacancies on the one hand, and a small volume of the object (film), on the other hand.

One should not exclude the possibility that the existence of a system of temperature peculiarities is a result of quantization of thermal vibration energy of atoms and can be attributed to the manifestation of a

quantum character of phonon spectra with decreasing size of the system (quantum size effect). The fact that the mentioned temperature anomalies are not observed in bulk crystals even at a high concentration of cation vacancies proves this suggestion.

Acknowledgements

References

[1] Abrikosov NH, Shelimova LE. Semiconducting materials based on A^4B^6 compounds. Moscow: Nauka; 1975. p. 40 [in Russian].

[2] Dresselhaus MS, Yu-Ming Lin, Koga T, Cronin SB, Rabin O, Black MR, Dresselhaus G. Low dimensional thermoelectricity. In: Tritt TM, editor. Semiconductors and semimetals: recent trends in thermoelectric materials research III. San Diego: Academic Press; 2001.

[3] Rogacheva EI, Gorne GV, Zhigareva NK, Ivanova AB. Homogeneity region of tin monotelluride. Inorg Mater 1991;27(2):194–7.

[4] Littlewood PB. Phase transitions and optical properties of IV–VI compounds. Lect Notes Phys 1982;152:238–46.

[5] Suski T. Phase transitions and resistivity anomalies in (Pb, Sn, Ge)Te compounds. Mater Sci 1985;11:3–53.

[6] Nashchekina ON, Rogacheva EI, Fedorenko AI. Phase transition in SnTe and temperature anomalies of kinetic properties. Functional Mater 1999;6(4):653–7.

[7] Nashchekina ON, Rogacheva EI, Fedorenko AI. Phase transitions and transport properties in the SnTe crystals and thin films. Proc SPIE 1999;3890:363–9.

[8] Nashchekina ON, Isakina AP, Prokhvatilov AI, Rogacheva EI, Fedorenko AI. Low temperature lattice instability of SnTe. Low Temperature Phys 1999;5(4): 390–5.

[9] Bashkirov ShSh, Dobrjakov IA, Liberman AB, Tsarevskiy SS. Mossbauer and X-ray investigations of the high-temperature phase transition in SnTe. Kristalographiya 1985;(30):1016–7.

[10] Khandozhko AG, Slinko EI, Letjuchenko SD, Tovstjuk KD. NMR temperature instability in SnTe. Ukrain Phys J 1978;(23):1747–9.

[11] Nashchekina ON, Rogacheva EI. Temperature anomalies of transport properties in SnTe epitaxial thin films. Phys Stat Sol A 1998;169(1):235–8.

[12] Balagurova EA, Grekov YuB, Semikolenova NA, Kharitonovskiy. In: Venevtsev YuN, Muromtsev VI, editors. Systems of peculiar temperature points of solids. Moscow: Nauka; 1986.

[13] Zorchenko VV, Sapelkin VP, Udovenko AA. Universal correlation of field and temperature dependences of conductivity of metallic island-like films. Fiz Tverd Tela 1990;32(3):905–8.

[14] Fedorenko AI, Zorchenko VV, Sipatov AYU, Mironov OA, Chistyakov SV, Nashchekina ON. Oscillations and quantization of resistivity in peculiar temperature points of threelayer PbS-PbTe-PbS films on (0 0 1)KCl. Fiz Tverd Tela 1999;41(9):1693–6.

[15] Rogacheva EI, Nashchekina ON, Korzh IA, Voinova LG, Krivulkin IM. Temperature dependencies of electrical resistivity and thermoelectric power in SnTe thin films. SPIE 2000;3950:1944–50.

[16] Venevtsev YuN, Muromtsev VI, Solov'ev SP. Establishment of correlation between temperature peculiarities and system of energy levels of materials. Dokl Akad Nauk SSSR 1976;230:121–4.