JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 9No 5, 05004(6pp) (2017)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 9 № 5, 05004(6cc) (2017)

# Kinetic Phenomena and Thermoelectric Properties of Polycrystalline Thin Films Based on PbSnAgTe Compounds

M.A. Ruvinskii, O.B. Kostyuk*, B.S. Dzundza, I.P. Yaremiy, M.L. Mokhnatskyi, Ya.S. Yavorskyy

*Vasyl Stefanyk Precarpathian National University 57, Shevchenko Str., 76025 Ivano-Frankivsk, Ukraine*

(Received 11 July 2017; revised manuscript received 16 July 2017; published online 16 October 2017)

Thin polycrystalline films based on PbSnAgTe (LATT) compounds on mica-muscovite substrates are obtained. The dependences of conductivity, mobility of current carriers and specific thermoelectric power on temperature for these condensates are investigated. It is established that the mechanisms of transport of carriers on the intergrain boundaries dominate at low temperatures, and at higher temperatures the charge transport is determined by the volume of grain. The predominant scattering mechanism at higher temperatures is scattering on acoustic phonons.

**Keywords:** Kinetic effects, Polycrystallites, Intergranular boundaries, Barriers, Thin films, LAST, Thermoelectric properties.

DOI: 10.21272/jnep.9(5).05004 PACS numbers: 73.50.-h, 73.50.Lw

## 1. INTRODUCTION

Trends in the development of modern society require solving the problem of energy supply. One of the ways to solve this problem is to find efficient materials for thermoelectric modules.

Lead telluride is already well known thermoelectric material. It is used for the medium-temperature region (500-750) K and for the sources and sensors of infrared radiation of the optical spectrum. This material is widely investigated both in the form of massive samples (single crystals, polycrystalline form, porous material) and in the form of thin films and one-dimensional structures. In addition, the lead telluride has been a model object for the study of physical processes in semiconductors for many years [1-3].

Doping and creating solid solutions based on PbTe allows you to obtain material with new properties. Thus, on the basis of PbTe, a new thermoelectric material PbAgSbTe, called LAST with a high thermoelectric figure of merit 2.2 at 800K, was obtained [4]. There is a large number of modifications of compounds LAST: LASTT ($Ag(Pb_{1-x}Sn_x)_mSbTe_{2+m}$), $Na_{1-x}Pb_mSb_yTe_{m+2}$ (SALT), and $Pb_{1-x}Sn_xTe$-PbS. The thermoelectric properties of these compounds are very sensitive to chemical composition. These materials, both n-and p-type, can be obtained by regulating of the chemical composition, which makes the system particularly promising for use in the production of electricity [5].

It should also be noted, that in many studies it was shown that in the polycrystalline films of lead chalcogenides, the Zeebeck coefficient S is larger than those for bulk samples with the same concentration of current carriers. This is due to the scattering on potential barriers at the grain boundary [6, 7].

In this paper, the films based on PbSnAgTe (LATT) compounds on fresh chips (0001) mica-muscovite substrates are obtain by vapor-phase methods and the regularities of changing their thermoelectric parameters from temperature and chemical composition are research. The dependence of chemical composition of PbAgSnTe compounds provides a perspective for application in various spheres of industry.

In the foregoing work [8], the patterns of the change of the thermoelectric parameters of films on the basis of the compounds of PbSnAgTe from their thickness, obtained from the vapor phase on the substrates of fresh chips (0001) mica-muscovite, were investigated.

The mechanisms of the transport of current carriers to the intersgrain boundaries of the polycrystalline films of *p*-CdTe, grown on glass substrates, are discussed in detail in [9]. The authors determined the energy of intergrain potential boundaries of 0.09 eV for *p*-CaTe films.

## 2. EXPERIMENT

Films for research are received by vapor deposition of synthesized material $Pb_{14}Sn_4Ag_2Te_{20}$, $Pb_{16}Sn_2Ag_2Te_{20}$ та $Pb_{18}Ag_2Te_{20}$ in a vacuum on the substrate of fresh chips (1000) of mica-muscovite. The temperature of the evaporator was $T_e = 870$ K and the temperature substrates $T_s = 470$ K. The thicknesses of the films are set by the deposition time within (1-3) min and are measured by microinterferometer MII-4 using digital image processing methods.

Measurement of electrical parameters of the films was on air at temperatures from 77 K to 300 K and at constant magnetic field on the automated device. It provides a process for measuring electrical parameters and initial registration and processing of data. The installation has the ability to construct graphs of time and temperature dependencies. Measured sample had four Hall contacts and two current contacts. As the ohmic contacts was used a silver film. The current through the sample was ≈ 1 mA. The magnetic field was directed perpendicular to the film surface. The induction of magnetic field was 1.2 Tesla.

For measurement of the Seebeck coefficient *S* was used the integral method. One end of the film had a constant temperature and the temperature of the other end was changed. The ends of the film attached to the

---

* oksanakostuk@gmail.com

massive copper plates to provide a constant temperature. For measurement of the temperature were used platinum thermoresitors. Measurement error is not more than 5 %. Type of carriers was defined by the sign of $R_H$ and $S$.

## 3. MICROSTRUCTURE OF FILMS

The electrical properties of films strong depend on their microstructure. One of the methods for studying of the microstructure of films is the diffraction analysis. The X-ray analysis of PbSnAgTe films are performed on a diffractometer DRON-3 (Cu$K_\alpha$-radiation, $\lambda = 0.1542$ nm, 30 kV, 15 mA) in the range of angles $15^o \leq 2\theta \leq 65^o$ with the scan step $0.05^o$. The size of coherent scattering region (CSR) was calculated according to the Debye-Sherrer formula [10]:

$$D = \frac{K_{hkl}\lambda}{\beta \cos\theta}, \tag{1}$$

where $\beta$ is the integral width of the diffraction peak at half height, λ is the wavelength of the Cu$K_\alpha$-radiation ($\lambda = 0.1542$ nm), $\theta$ – the diffraction angle, $D$ – the size of the coherent scattering region (CSR), nm, and $K_{hkl}$ is the dimensionless particle shape coefficient (Sherrer constant), which is determined by the inverse form of particles and indices ($hkl$) of diffraction reflection. For crystals with cubic symmetry, the coefficient $K_{hkl}$ for various Miller's crystallographic indices ($hkl$) of a cubic crystalline lattice is calculated by the formula [10]:

$$K_{hkl} = \frac{6|h|^3}{\sqrt{h^2+k^2+l^2}\left(6h^2-2|hk|+|kl|+2|hl|\right)} \tag{2}$$

Figure 1 shows the X-diffractograms of the films based on the compounds PbSnAgTe on the mica-muscovite substrate obtained in this study. It is seen that all samples are polycrystalline with a cubic structure (spatial group Fm3m). The most intense reflexes for all studied compositions are (200) and (222).

The diffraction peak (222) was chosen to study the size of the CSR, since the peak (200) for the films merges with a similar orientation for the mica (Fig.1.2). The full width at half of height of maximum (FWHM) for the peak (222) for the film of the composition $Pb_{14}Sn_4Ag_2Te_{20}$ is 0.31°, for $Pb_{16}Sn_2Ag_2Te_{20}$ – 0.21°, and for $Pb_{18}Ag_2Te_{20}$ – 0.25°. According to Debye-Scherer formula, the calculated of the size of the crystallite for a film of the composition of $Pb_{14}Sn_4Ag_2Te_{20}$ is 36.2 nm, for $Pb_{16}Sn_2Ag_2Te_{20}$ – 53.6 nm, and for $Pb_{18}Ag_2Te_{20}$ – 45.4 nm.

The value of the Shererr constant for the crystallographic plane (222) is $K_{222} = 1.1547$.

The diffraction pattern of mica-muscovite, which was used as substrates for investigated films, is shown in Fig. 2. Mica has a monoclinic crystalline structure with a slight deviation from cubic symmetry. The diffractograms of the samples illustrate the predominant orientation (111), which indicates the partial epitaxial growth of the PbSnAgTe films on the mica substrate. Consequently, there is a crystallographic correspondence between the

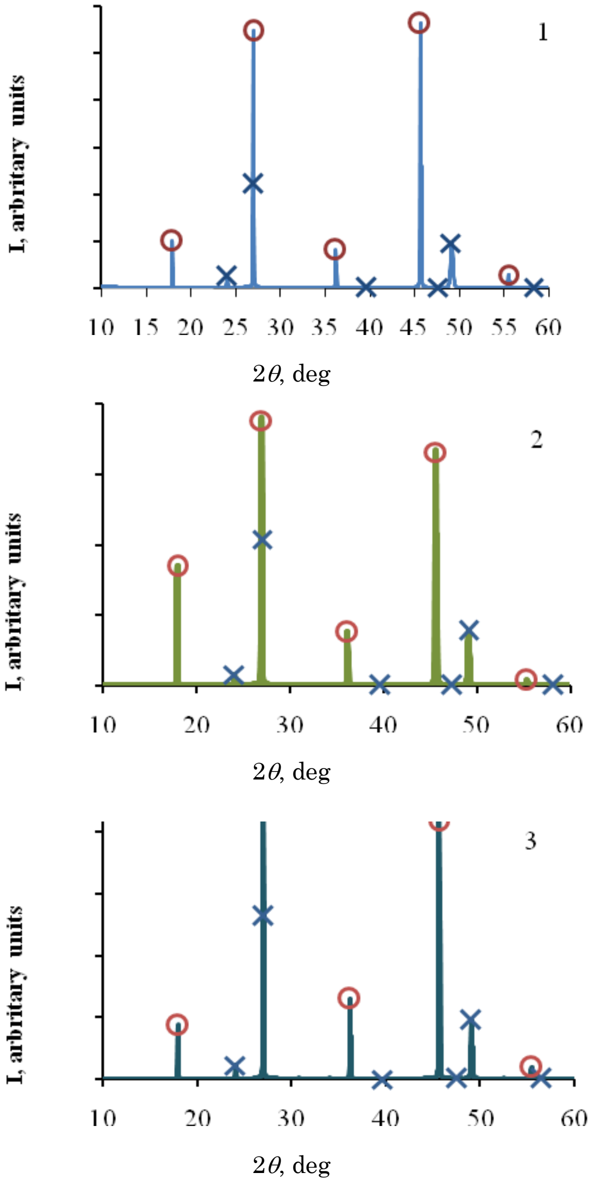

**Fig. 1** – X-ray diffractograms of films on mica-muscovite substrates based on compounds PbSnAgTe of composition: $Pb_{14}Sn_4Ag_2Te_{20}$ (1), $Pb_{16}Sn_2Ag_2Te_{20}$(2) $Pb_{18}Ag_2Te_{20}$(3). ○ – peaks corresponding to mica-muscovite, × - peaks corresponding to the material

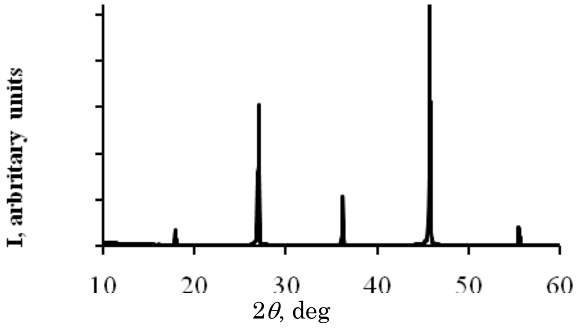

**Fig. 2** – X-ray diffractograms of mica-muscovite, which are used as substrates

substrate and the film (that is, certain crystallographic planes and directions are parallel).

## 4. ANALYSIS OF ELECTRICAL PROPERTIES

Electronic transport of current carriers in polycrystalline films is determined both by crystallites and by intergrain barriers. If the structure of the crystallites is ordered, the intergrain boundaries are disordered. According to Fig. 1, the part of the film corresponding to the grain is a region with direct bands, and on the boundaries of crystallite there is a symmetrical bending of the bends. If we take into account the nature of the boundaries of the grain, then according to the model proposed in [11, 12], the electronic properties of the polycrystal are determined by the capture of the carriers by torn bonds of atoms, which are localized within the intergrain boundaries. For the barrier region two main mechanisms of charge transfer are considered: thermoelectric over-barrier emission and subbarrier tunnel transport.

Full current through polycrystal is determined both by the conductivity of the crystallites and by the mechanism of the transition of carriers from one crystallite to another, that is, the conductivity of the intergrain boundaries. As a rule, the specific conductivity of crystallites is practically equal to the specific conductivity of a monocrystal of this material. Consequently, in general, transport properties of polycrystals are determined by the peculiarities of electronic transport in the barrier region.

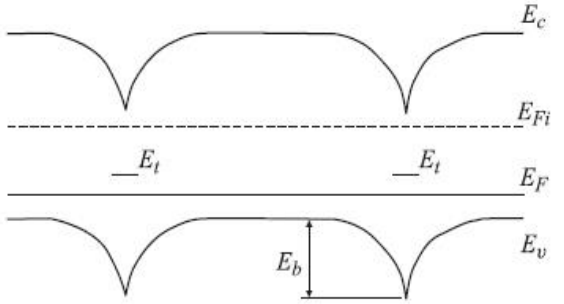

**Fig. 3** – The band model of the grain boundary in the polycrystals of the p-type conductivity, $E_c$ – the edge of the conduction band, $E_v$ – the edge of the valence band, $E_t$ – level of traps, $E_{Fi}$ – the Fermi level in an intrinsic semiconductor, $E_b$ – the height of the energy barrier

Tunnel currents are significant in the case of very narrow barriers, for example, in highly doped polycrystals. In slightly doped polycrystals tunnel currents are small compared with the currents of electronic emission.

The current density, when the voltage U applied to barrier, is equal [11]:

$$j = \frac{q^2 p}{\sqrt{2\pi m^* kT}} U e^{-\frac{qV_b}{kT}} \qquad (3)$$

where $qV_b = E_b$, $V_b$ – the potential of the barrier, $q$ – the charge of the electron, $T$ – the temperature, $k$ – Boltzmann constant, $m^*$ – effective mass, $p$ – concentration of the carriers.

From formula (3), the conductivity of a polycrystal with a crystallite size $L$ will be determined as:

$$\sigma = \frac{Lq^2 p}{\sqrt{2\pi m^* kT}} e^{-\frac{qV_b}{kT}}. \qquad (4)$$

Taking into account that

$$\sigma = q\mu p \qquad (5)$$

the effective value of mobility will be

$$\mu = \frac{Lq}{\sqrt{2\pi m^* kT}} e^{-\frac{E_b}{kT}}. \qquad (6)$$

The dependences of the electrical conductivity σ, the concentration of current carriers n, p, the Seebeck coefficient S and the thermoelectric power $S^2\sigma$ on the temperature of the films based on PbSnAgTe compounds on the mica substrates are shown in Fig. 4-8. These dependences can be explained by the mechanisms of scattering of current carriers on acoustic phonons and grain boundaries.

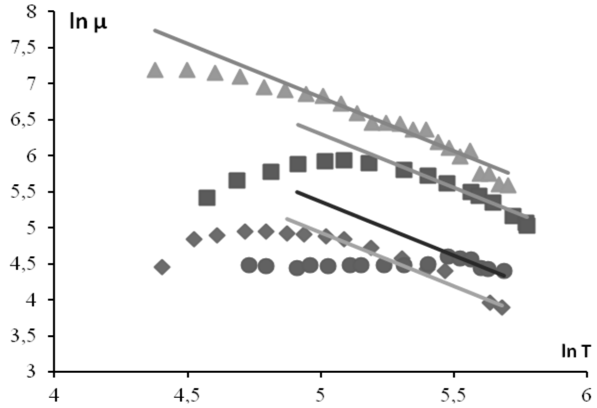

**Fig. 4** – The dependence of the logarithm of mobility ln$\mu$ on the logarithm of temperature for the films of composition: ▲ – PbTe, ■ – $Pb_{14}Sn_4Ag_2Te_{20}$, ♦ – $Pb_{16}Sn_2Ag_2Te_{20}$, ● – $Pb_{18}Ag_2Te_{20}$ on fresh chips (0001) of mica-muscovite. Points – experiment, lines – approximation by the formula (7)

The temperature dependence of the mobility of charge carriers is directed in the coordinates ln$\mu$ of ln $T$ (Fig. 4). It is clear that all graphs at higher temperatures have a slope coefficient very close to – 3/2. It can be concluded that the main mechanism of carrier scattering is the scattering on acoustic phonons [13]. This behavior for thin films of $p$-PbTe was observed by the authors in work [14].

The mobility of carriers (in this case, holes) due to scattering on long-wave acoustic oscillations, with taking into account the temperature dependence of the effective mass, is determined by the formula

$$\mu_a = m^{*-5/2} T^{-3/2} \qquad (7)$$

The most informative parameter that characterizes the barrier mechanism of electronic transport is the Hall mobility. In polycrystalline films, the tunneling transport of charge carriers is observed at low temperatures in films with a high concentration of doping impurities, which reduces the barrier width. The contribution of the subbarrier tunneling is appears in decreasing of the slope of the curves $\mu = f(1/T)$ та $\sigma = f(1/T)$ with decreasing of temperature. The decrease of mobility with decrease of temperature is observed for the samples under study at temperatures $T < 150$ K (Fig. 5). Especially clearly this is observed for films composition $Pb_{14}Sn_4Ag_2Te_{20}$ та $Pb_{16}Sn_2Ag_2Te_{20}$, because the condition of high content of impurities is fulfilled. Therefore, the probability of tunneling will be greater, because the width of the potential barrier decreases with increasing concentration of the impurity. For the composition $Pb_{18}Ag_2Te_{20}$, the slope of the straight line is rather small, therefore the implementation of the over-barrier thermoelectronic emission is possible.

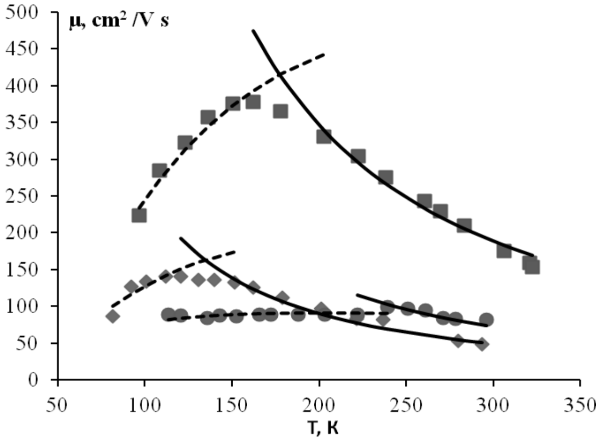

**Fig. 5** – Dependence of mobility μ on temperature $T$ for the films of composition: ■ – $Pb_{14}Sn_4Ag_2Te_{20}$, ♦ – $Pb_{16}Sn_2Ag_2Te_{20}$, ● – $Pb_{18}Ag_2Te_{20}$ on fresh chips (0001) of mica-muscovite. Points – experiment, solid line – scattering on acoustic phonons, dashed line – scattering on the boundaries of the grains

Dependence $\ln(\mu \cdot T^{1/2}) = f(1/T)$ (7) was considered to find the energy of a potential barrier on the grain boundary. By the slope of the line was determined the activation energy $E_\mu$, considering that $E_\mu = E_b$. The results of the calculation are given in Table 1. As can be seen, the energy of the barrier increases with an increase in the content of the Stanum.

**Table 1** – The height of the potential barrier $E_b$ for films PbSnAgTe

| Composition | Film thickness $d$, nm | The height of the potential barrier $E_b$, eV |
|---|---|---|
| $Pb_{14}Sn_4Ag_2Te_{20}$ | 540 | 0.0161 ± 0.0003 |
| $Pb_{16}Sn_2Ag_2Te_{20}$ | 810 | 0.0132 ± 0.0017 |
| $Pb_{18}Ag_2Te_{20}$ | 540 | 0.0087 ± 0.0006 |

Increasing the activation energy - intergranular potential barriers can be explained by the realization of the condition when the crystallites are completely depleted on the carrier, and the traps only partially filled. Then the height of the potential barrier $V_b$ increases linearly with increasing of the concentration n in agreement with the expression [11]:

$$V_b = \frac{qL^2 n}{8\varepsilon}.$$

where $\varepsilon$ is the dielectric permittivity.

Thus, an increase in the concentration of p-type carriers (Fig. 7) leads to an increase in the height of potential barriers on intergrain boundaries.

The dependence of conductivity on temperature for different compositions of PbSnAgTe compounds is shown in Fig. 6. For the compositions $Pb_{16}Sn_2Ag_2Te_{20}$ and $Pb_{18}Ag_2Te_{20}$, an activation mechanism of conductivity is observed. That is, conductivity increases with increasing of the temperature. In the temperature range $T > 170$ K for the composition $Pb_{14}Sn_4Ag_2Te_{20}$, as in pure PbTe (Fig.6), the decrease in conductivity with increasing temperature is explained by the decrease in mobility, since the concentration for this sample is weakly dependent on the temperature in this temperature range: $\sigma = ep\mu$ [15].

In Fig. 7 shows the dependence of the Hall concentration of current carriers $n$, $p$ on temperature. The investigated compositions have different types of conductivity: $Pb_{14}Sn_4Ag_2Te_{20}$ and $Pb_{16}Sn_2Ag_2Te_{20}$ – $p$-type, $Pb_{18}Ag_2Te_{20}$ – $n$-type. This is confirmed by measurements of the Zeebeck coefficient $S$ (Fig. 8). The impurity of silver in the plumbum telluride shows a weak acceptor effect. This is confirmed by the fact that the electrical conductivity of $Pb_{18}Ag_2Te_{20}$ samples is less than that of pure $n$-PbTe films on mica (Fig. 6), but the transition to the $p$-type does not occur. With the introduction of Sn obtain $p$-type conductivity. Moreover, with increasing content of the Sn, the concentration of carriers increases (Fig. 7).

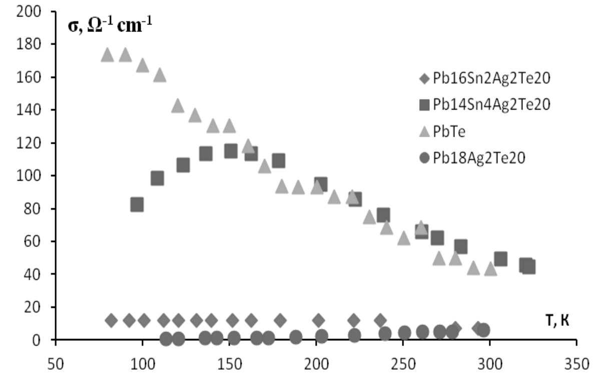

**Fig. 6** – Dependence of conductivity σ on temperature $T$ for the films of composition: ▲ – PbTe, ■ – $Pb_{14}Sn_4Ag_2Te_{20}$, ♦ – $Pb_{16}Sn_2Ag_2Te_{20}$, ● – $Pb_{18}Ag_2Te_{20}$ on fresh chips (0001) of mica-muscovite

The thermoelectric power $S^2\sigma$ and Zeebeck coefficient S increase with increasing temperature (Fig. 8, 9) for all studied compositions. Moreover, it is the largest for the films of composition $Pb_{14}Sn_4Ag_2Te_{20}$ due to the high values of the Zeebeck coefficient and conductivity.

Note that for massive samples, from which films were obtained, the material of the composition $Pb_{14}Sn_4Ag_2Te_{20}$ had the lowest thermal conductivity

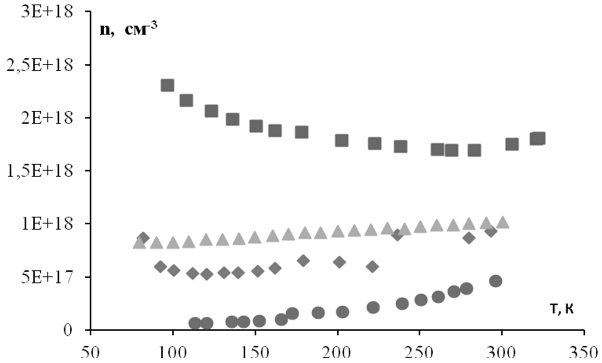

**Fig. 7** – Dependence of Hall concentration on temperature $T$ for the films of composition: ▲ – PbTe, ■ – $Pb_{14}Sn_4Ag_2Te_{20}$, ♦ – $Pb_{16}Sn_2Ag_2Te_{20}$, ● – $Pb_{18}Ag_2Te_{20}$ on fresh chips (0001) of mica-muscovite

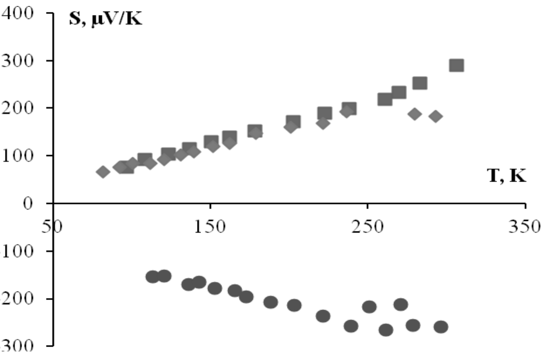

**Fig. 8** – Dependence of the Zeebeck coefficient S on temperature $T$ for the films of composition: ■ – $Pb_{14}Sn_4Ag_2Te_{20}$, ♦ – $Pb_{16}Sn_2Ag_2Te_{20}$, ● – $Pb_{18}Ag_2Te_{20}$ on fresh chips (0001) mica-muscovite

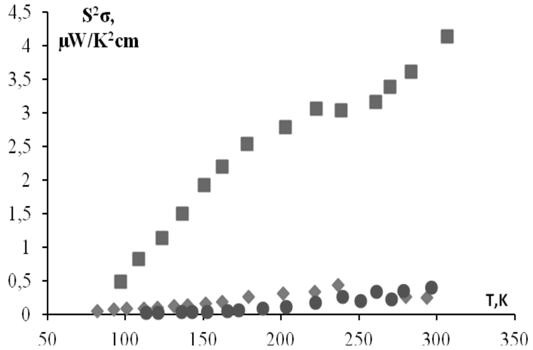

**Fig. 9** – Dependence of specific thermoelectric power $S^2\sigma$ on temperature $T$ for the films of composition: ■ – $Pb_{14}Sn_4Ag_2Te_{20}$, ♦ – $Pb_{16}Sn_2Ag_2Te_{20}$, ● – $Pb_{18}Ag_2Te_{20}$ on fresh chips (0001) mica-muscovite

$\varkappa = 3\cdot10^{-3}$ W/(cm·K). This makes it possible to assume that films based on this chemical composition will be characterized by high thermoelectric figure of merit. Therefore, films based on Pb14Sn4Ag2Te20 can be used as $p$-branches of high-performance thermoelectric energy converters.

## 5. CONCLUSIONS

1. The dependences of thermoelectric properties on temperature for thin films on the basis of the compounds $Pb_{14}Sn_4Ag_2Te_{20}$, $Pb_{16}Sn_2Ag_2Te_{20}$ and $Pb_{18}Ag_2Te_{20}$ obtained on mica substrates are investigated.
2. It was shown that the films based on the compounds $Pb_{14}Sn_4Ag_2Te_{20}$ have the highest specific thermoelectric power in comparison with other studied compositions.
3. It was established that the mechanisms of transport of current carriers at intergrain boundaries dominate at low temperatures, and at higher temperatures, the transport of charge is determined by the volume of grain. The predominant scattering mechanism at higher temperatures is scattering by acoustic phonons.

Publications are based on the research provided by the grant support of the State Fund for Fundamental Research (project No F73/38-2017).

---

## Кинетические явления и термоэлектрические свойства поликристаллических тонких пленок на основе соединений PbSnAgTe

М.А. Рувинский, О.Б. Костюк, Б.С. Дзундза, И.П. Яремий, М.Л Мохнацкий, Я.С. Яворский

*Прикарпатский национальный университет имени Василия Стефаника,*
*ул. Шевченка, 57, 76000 Ивано-Франковск, Украина*

В работе получены тонкие поликристаллические пленки на основе соединений PbSnAgTe (LATT) на подложках из слюды-мусковит. Исследована зависимость проводимости, подвижности носителей тока и удельной термоэлектрической мощности от температуры данных конденсатов. Установлено, что механизмы переноса носителей тока на межзеренних границах доминируют при низких температурах, а при более высоких температурах перенос заряда определяется объемом зерна. Преобладающим механизмом рассеяния при высоких температурах является рассеяние на акустических фононах.

**Ключевые слова**: Кинетические эффекты, Поликристалиты, Межзеренние границы, Барьеры, Тонкие пленки, LAST, Термоэлектрические свойства.

# Кінетичні явища та термоелектричні властивості полікристалічних тонких плівок на основі сполук PbSnAgTe

М.А. Рувінський, О.Б. Костюк, Б.С. Дзундза, І.П. Яремій, М.Л Мохнацький, Я.С. Яворський

*Прикарпатський національний університет імені Василя Стефаника,*
*вул. Шевченка, 57, 76000 Івано-Франківськ, Україна*

В роботі отримано тонкі полікристалічні плівки на основі сполук PbSnAgTe (LATT) на підкладках зі слюди-мусковіт. Досліджено залежність провідності, рухливості носіїв струму та питомої термоелектричної потужності від температури для даних конденсатів. Встановлено, що механізми перенесення носіїв струму на міжзеренних межах домінують при низьких температурах, а при вищих температурах перенесення заряду визначається об'ємом зерна. Переважаючим механізмом розсіяння при вищих температурах є розсіяння на акустичних фононах.

**Ключові слова:** Кінетичні ефекти, Полікристаліти, Міжзеренні межі, Бар'єри, Тонкі плівки, LAST, Термоелектричні властивості**.**

## REFERENCES

1. E.M. Larramendi, O. Calzadillia, A. Gonzalez-Arias, E. Hernadzer, J. Ruiz-Garsia, *Thin Solid Films* **389**, 301 (2001).
2. M.A. Ruvinskii, O.B. Kostyuk, B.S. Dzundza, *J. Nano Electron. Phys.* **8** No 2, 02051 (2016)
3. M.A. Ruvinskii, D.M. Freik, B.M. Ruvinskii, V.V. Prokopiv, *Techn. Phys. Lett.* **26** No 8, 647 (2000).
4. H. Wang, J.-F. Li, C.-W. Nan, M. Zhou, W. Liu, B.-P. Zhang, T. Kita, *Appl. Phys. Lett.* **88**, 092104 (2006).
5. I. Horichok, R. Ahiska, D. Freik, L. Nykyruy, S. Mudry, O. Matkivskiy, T. Semko, *J. Electron. Mater.* **45** No 3, 1576 (2016).
6. K. Kishimoto, M. Tsukamoto, T. Koyanagi, *J. Appl. Phys.* **92** No 9, 5331 (2002).
7. Z. Dashevsky, R. Kreizman, M.P. Darieli, *J. Appl. Phys.* **98**, 094309-1 (2005).
8. B.S. Dzundza., O.B. Kostyuk, V.I. Makovyshyn, *PCSS* **17** No 3, 368 (2016).
9. S.A. Kolosov, Yu.V. Klevkov, A.F. Plotnykov, *Semicond.* **38** No **4**, 473 (2004).
10. A.I. Gusev, *Nanomateryaly, nanostruktury, nanotekhnolohyy* (Moskva: FIZMATLYT: 2009).
11. S. Schuler, S. Nishiwaki, J. Beckmann, N. Rega. S. Brehme, S. Siebentrittand M.Ch. Lux-, *Proc. 29th IEEE Photovoltaic Specialist Conf.* (New Orleans: 2002).
12. Yu.V. Klevkov, S.A. Kolosov, S.A. Medvedyev, A.F. Plotnykov, *Semicond.* **35**, 1139 (2001).
13. O.V. Tretyak, V.Z. Lozovs'kyy. *Osnovy fizyky napivprovidnykiv* (Kyyiv: Kyyivs'kyy universytet: 2007).
14. U.P. Khairnar, S.S. Behere, and P.H. Pawar, *J. Chem., Biologi. Phys. Sci.* **2** No 8, 1529 (2012).
15. P.Y. Yu, M. Cardona, *Fundamentals of Semiconductors: Physics and Materials Properties* (Springer: 2010).