D.M. Freik, B.S. Dzundza, V.I. Makovyshyn, L.Yo. Mezhylovska, V.I. Bachuk

¹Vasyl Stefanyk Precarpathian National University, 57, Shevchenko Str., Ivano-Frankivsk, 76018, Ukraine

THERMOELECTRIC PROPERTIES OF VAPOUR-PHASE CONDENSATES BASED ON DOPED LEAD TELLURIDE *SnTe:Bi*

Thermoelectric properties of vapour-phase condensates based on doped tin telluride SnTe:Bi of different composition obtained in open vacuum on glass ceramic and mica substrates are investigated. It is shown that thin films on fresh (0001) cleavages of muscovite mica with the content of ~ 0.3 mol.% Bi are characterized by maximum values of thermoelectric power ~ 42 μ W/K²cm. **Key words:** thin films, tin telluride, doping, thermoelectric properties.

Introduction

Tin telluride is widely used in semiconductor engineering. It also offers great promise as thermoelectric material for medium-temperature range (500 - 750 K) [1, 2, 3]. Preparation of thin film material extends considerably the limits of practical application. The problem of temporal stability of electrical parameters remains to be solved. Moreover, on exposure to air, a layer enriched with *p*-type conductivity carriers is formed on the film surface due to the acceptor effect of oxygen [4].

This paper studies the thickness dependences of thermoelectric parameters of films based on pure and bismuth doped SnTe obtained from the vapour phase on glass ceramic and mica substrates.

Experimental procedure

Films for investigation were prepared by vapour deposition of synthesized *SnTe* material in vacuum onto the substrates of fresh (0001) cleavages of muscovite mica and glass ceramic. The temperature of evaporator was $T_{ev} = 870$ K, and substrate temperature $T_{sub} = 470$ K. Film thickness was assigned by deposition time within (5 – 480 s) and measured by interference microscope MII-4.

The electric parameters of the films were measured in the air at room temperatures in constant magnetic fields on the elaborated automated installation assuring both the process of electric parameters measurement and recording and primary data processing, with the possibility of constructing the plots of time and temperature dependences. The sample being measured had four Hall and two current contacts. As the ohmic contacts, silver films were used. Current through the samples was ≈ 1 mA. Magnetic field was directed perpendicular to the surface of films at induction of 1.5 T.

The results of investigation and the thickness dependences of electric conductivity σ , the Hall concentration of current carriers n_H and the Seebeck coefficient *S* are represented in Figs. 1 – 2.

Analysis of the results of investigation

The introduction of *Bi* leads to donor effect in tin telluride which is manifested in decreasing hole concentration in the bulk of the films. The results of investigation of thermoelectric parameters of vapour-phase condensates based on doped tin telluride for different compositions are given in the Table. With increasing content of doping impurity, the thermoelectric power is first increased, and

then drastically decreased, which is due to overrunning of Bi solubility region in SnTe. Maximum thermoelectric power is achieved with impurity content about 0.3 mol.%, but for condensates prepared on fresh (0001) cleavages of muscovite mica it is much higher than for samples on glass ceramic.

Table

mol.% <i>Bi</i>	$\sigma, \Omega^{-1} cm^{-1}$	μ , cm ² /V·s	n, cm^{-3}	<i>S</i> , μV/K	$S^2 \sigma$, $\mu W/K^2 \cdot cm$
Films 0.1 µm thick on fresh (0001) cleavages of muscovite mica					
0	2790	32	$5.44 \cdot 10^{20}$	55	8.4
0.3	3900	146	$1.67 \cdot 10^{20}$	90	31.2
1.5	3904	278	$8.78 \cdot 10^{19}$	65	16.3
2	852	56	9.56·10 ¹⁹	131	14.6
Films 0.5 μ m thick on fresh (0001) cleavages of muscovite mica 0.5 μ m					
0	1414	61	$1.44 \cdot 10^{20}$	31	1.3
0,3	2780	221	$7.87 \cdot 10^{19}$	54	8.1
1,5	5501	318	$1.08 \cdot 10^{20}$	56	17.5
2	674	68	$6.18 \cdot 10^{19}$	123	10.2
Films 2 µm thick on fresh (0001) cleavages of muscovite mica					
0	1156	74	$9.71 \cdot 10^{19}$	20	0.5
0,3	2570	242	6.63·10 ¹⁹	44	4.9
1,5	5800	323	$1.12 \cdot 10^{20}$	55	17.7
2	641	71	$5.62 \cdot 10^{19}$	121	9.3
Films 0.05 µm thick on glass-ceramic substrates					
0	4815	19	$1.55 \cdot 10^{21}$	64	19.8
0.3	5776	102	$3.54 \cdot 10^{20}$	62	22.3
1.5	1390	82	$1.05 \cdot 10^{20}$	80	8.8
Films 0.3 µm thick on glass-ceramic substrates					
0	1844	47	$2.44 \cdot 10^{20}$	34	2.1
0.3	4129	257	$1.01 \cdot 10^{20}$	30	3.7
1.5	4398	170	$1.62 \cdot 10^{20}$	15	0.9
Films 1 µm thick on glass-ceramic substrates 1 µm					
0	1428	60	$1.48 \cdot 10^{20}$	19	0.5
0.3	3899	289	8.43·10 ¹⁹	23	2.1
1.5	4819	174	$1.73 \cdot 10^{20}$	12	0.7

Thermoelectric parameters of vapour-phase condensates based on doped tin telluride of different composition

Figs. 1-2 show the thickness dependences of thermoelectric parameters of vapour-phase SnTe

condensates with the content of bismuth 0.3 mol.%. It is seen that with reduction of condensate thickness *d*, irrespective of composition, conductivity grows considerably, and for thicknesses more than $d \approx 0.5 \,\mu\text{m}$ it is practically unvaried. This is related to growth of the concentration of current carriers in the range of small film thicknesses, due to the acceptor effect of surface-adsorbed oxygen. And current carrier concentration for pure telluride is higher than for doped one due to the donor effect of bismuth. With decreasing thickness of films prepared on mica substrates, the Seebeck coefficient is increased as well, which results in considerable increase of thermoelectric power (Fig. 1, *d*).



Fig. 1. Dependences of electric conductivity σ (a), the Hall concentration n (b), the Seebeck coefficient S (c) and thermoelectric power $S^2\sigma$ (d) on thickness d of SnTe:Bi films on fresh (0001) cleavages of muscovite mica. The content of Bi is 0.3 mol.%.

Films prepared on fresh (0001) cleavages of muscovite mica are characterized by considerably higher thermoelectric power due to double Seebeck coefficient than samples prepared on glass ceramic (Figs. 1 – 2, d), owing to better structural order at the cost of orientation effect of the substrate. For condensates obtained on glass ceramic substrates the thickness dependences of the Seebeck coefficient and thermoelectric power have a distinct maximum in the range of thicknesses $\sim 0.6 \,\mu\text{m}$ (Fig 2, c, d) which is due to manifestation of size effects with small condensate thicknesses.



Fig. 2. Dependences of electric conductivity σ (a), the Hall concentration n (b), the Seebeck coefficient S (c) and thermoelectric power $S^2\sigma$ (d) on thickness d of SnTe:Bi films on glass-ceramic substrates. The content of Bi is 0.3 mol.%.

On the whole, high conductivity values combined with considerable Seebeck coefficient value of SnTe:Bi films yield thermoelectric material of *p*-type conductivity which is promising for construction of film micromodules for thermoelectric power conversion.

Conclusions

- 1. Thermoelectric properties of vapour-phase thin films of lead telluride doped with bismuth, prepared by vapour-phase methods on glass-ceramic and mica substrates have been studied.
- 2. It has been shown that p-type SnTe thin films have improved thermoelectric parameters as compared to the bulk samples.
- 3. Doping of tin telluride with bismuth, despite some reduction of conductivity allows improving thermoelectric power due to the Seebeck coefficient increase.

The work has been performed in conformity with a comprehensive scientific project of Ukrainian State Foundation for Basic Research (state registration number 0113U003689) and the NAS of Ukraine (state registration number 0110U006281).

References

- 1. V.M. Shperun, D.M. Freik, and R.I. Zapukhlyak, *Thermoelectricity of Lead Telluride and its Analogs* (Ivano-Frankivsk: Plai, 2000), 250 p.
- 2. D.M. Freik, M.A. Haluschak, and L.I. Mezhylovska, *Physics and Technology of Thin Films* (Lviv: Vyschaya Shkola, 1988), 182 p.
- 3. D.M. Freik, I.V. Gorichok, N.I. Dykun, and Yu.V. Lysyuk, Effect of manufacturing technique on the thermoelectric properties of nonstoichiometric and doped lead telluride and solid solutions on its basis, *J. Thermoelectricity* **2**, 42 49 (2011).
- 4. R.L. Petritz, Theory of an Experiment for Measuring the Mobility and Density of Carriers in the Space-Charge Region of a Semiconductor Surface, *Phys. Rev.* **110**, 1254 (1958).

Submitted 30.05.14