$Bi_2Te_{2,7}Se_{0,3}$ CRYSTAL CONDUCTIVITY PECULIARITIES

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The conductivity of volume layered thermoelectric semiconductor of *n*-type conduction of $Bi_2Te_{2.7}Se_{0.3}$ intercalated by nickel ions and influence of crystallites of Van-der-Waals layer surfaces on thermo-e.m.f. and conductivity of material are investigated.

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INTRODUCTION

As it is known, nowadays $Bi_2Te_{2.7}Se_{0.3}$ layered crystals is the one of the most popular and required materials in thermoelectricity production.

The problem of thermo-electrics is low efficiency the value of which is characterized by parameter ZT:

$$ZT=\alpha^2 \cdot T/\rho\ \lambda, \qquad (1)$$

where α is Zeebek coefficient,
ρ is resistivity,
λ is thermal conductivity coefficient,
T is average temperature.

The nano-structurization is the perspective method of ZT increase [1].
It is carried out by the way of thermoelectric formation with ultra-fine-grain polycrystalline structure for volume materials. Such approach causes λ decrease because of phonon scattering on grain boundaries. Besides, the variation of grain sizes in nano-meter scale gives the additional degrees of freedom for optimization of other parameters including formula ZT [2].

The layered thermoelectric semiconductors with clusters of impurity atoms are of the big scientific and practice interest. This is connected with possibility of purposeful control by fundamental parameters of semiconductor materials and also with revealing of the unique physical phenomena in such materials allowing us to form the series of principally new electron devices on their base [3].

The topological isolators are the example of another approach to phase classification in physics of substance condensed state. Being semiconductors inside the volume, they present themselves new quantum state of substance, characterizing the specific edge or surface electron states. The peculiarity is the fact that their special electron properties are caused by volume crystal region, but they reveal on its surface in the form of state band crossing the fundamental forbidden gap. As a result, the surface of volume isolator acquires the metallic properties [4].

The investigations of electrophysical characteristics of cluster microstructure formed by nickel atoms in silicon structure are carried in work [5].

The doping of $Bi_2Te_{2,7}Se_{0,3}$ by bismuth for the compensation of electron excess concentration significantly decreases the anisotropy of micro- and macro- electric conductivity. The weakly expressed tendency to anisotropy increases of electric conductivity at decrease of electron concentration in conductivity band takes place [6].

The compensation method realized in work [7] which is excessive optimal electron concentration in extrude materials on the base of $Bi_2Te_{2,7}Se_{0,3}$ by the way of bismuth doping allows us to obtain the material with the properties (α, σ) suitable for their use at preparation of thermoelectric coolers.

The samples which are the foils of $Bi_2Te_{2.7}Se_{0.3}$ intercalated by nickel are obtained. X-ray phase analysis of the samples shows the composition crystallinity. $Ni_{1,297}Te$ new phase and Ni-Se-Te chains are revealed in the composition. The free nickel atoms aren't revealed in the composition.

The grains being the coalescence of spherical form of $Ni_{1.297}Te$ composition, are revealed with the help of scanning electron microscope in $Bi_2Te_{2.7}Se_{0.3}$<Ni> samples. The sample spalling on 1μm shows that their maximum sizes correspond to 500-600nm, they are evenly distributed throughout the volume on stages of layer breaks.

$Ni_{1.297}Te$ grains with minimal sizes corresponding to 35±5nm with number of atoms $n=10^6$. They can form the nano-rods along one line in layer plane. The self-organizations in double, triple, fourfold, grains form the nano-rods with sizes: 70, 100, 130nm.

Ni-Se-Te chains form in $Bi_2Te_{2,7}Se_{0,3}$ crystal layers and $Ni_{1,297}Te$ grains form in Van-der-Waals spaces at intercalation process by nickel ions.

That's why the investigations of charge transfer mechanism of layered $Bi_2Te_{2.7}Se_{0.3}$ intercalated by nickel is of the big scientific and practical interest.
The aim of the present work is the revealing role of *Ni* influence on conductivity mechanism of the majority charge carriers of layered $Bi_2Te_{2.7}Se_{0.3}$.

EXPERIMENT AND RESULTS

The single-crystal $Bi_2Te_{2,7}Se_{0,3}$ of *n*-type conduction is used as initial material. The investigated samples for electric measurements are prepared in such way that external constant electric field is applied

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crosswise to crystal natural layers, i.e., along *c* axis. The contact square is $10^{-2}cm^2$. The tetra-probe method is used. The contact ohmicity is checked by taking off VAC and potential distribution along the sample and vice versa. The argentum paste is used for the preparation of contacts to the investigated samples $Bi_2Te_{2,7}Se_{0,3}$<Ni>.

The introduction of nickel impurity by intercalation in quantity from 0,127 mass % up to 0,383 mass % in layer $Bi_2Te_{2,7}Se_{0,3}$ leads to insignificant decrease of the sample electric conductivity. This is possibly connected with the fact that introduced nickel impurity in the ion form taking vacant places of tellurium in quintet upper layer forms Ni-Se-Te chains. Simultaneously, nickel ions on defects near Van-der-Waals surface form the nano-crystals of $Ni_{1,297}Te$ grain.

The grain disposition in intercrystalline interlayers in direction of shift planes is caused by weak bond at big intervals between $Te^{(1)}$-$Te^{(1)}$ layers and leads to shunting of isolating layers, i.e., to small decrease of electric conductivity.

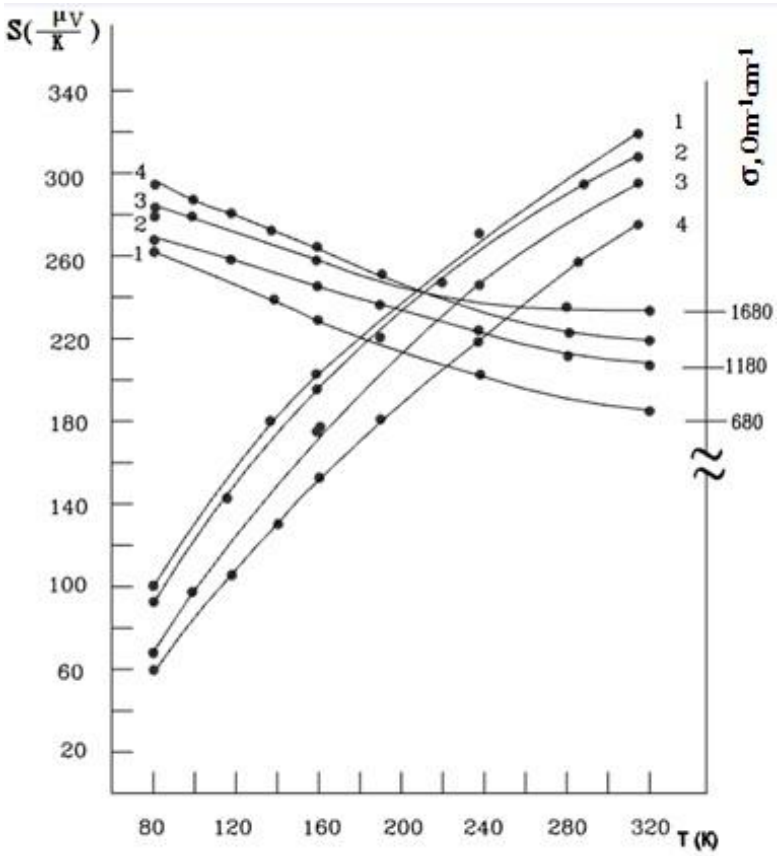

Fig. 1. The temperature dependence of thermo-e.m.f. and conduction for $Bi_2Te_{2,7}Se_{0,3}$ samples without impurity 4 with nickel impurity 1 is 0,127%, 2 is 0,383%, 3 is 0,688%.

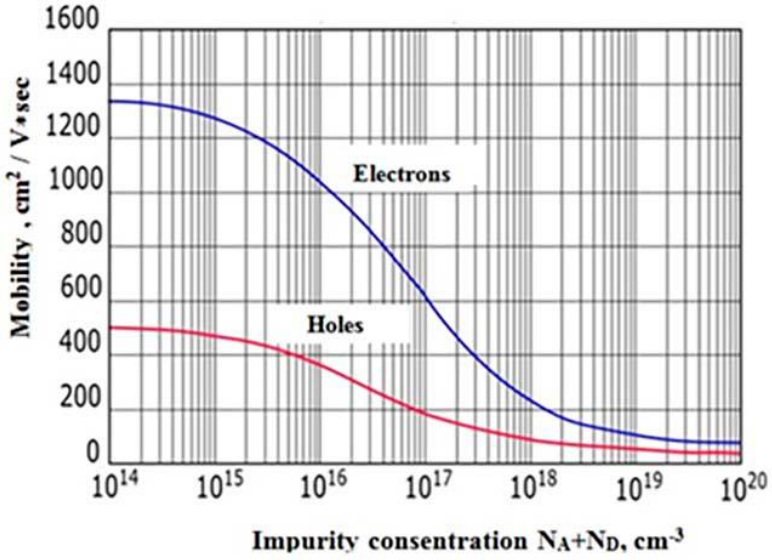

Fig.2. The mobility of electrons and holes in silicon at 300K [9].

The insignificant decrease of conductivity value that is connected with decrease of value of charge carrier mobility in the sample is observed in the figure. It is seen that curve of conductivity graph 2, 3 is below than the curve of pure sample 4.

The introduction of nickel impurity concentration 0,127% mass % in Van-der-Waals spaces $Bi_2Te_{2,7}Se_{0,3}$ forms Ni-Se-Te chains and nano-wire $Ni_{1,297}Te$ in crystals, leads to decrease of conduction value up to σ=680Om^{-1}cm^{-1} and is accompanied by increase of thermo-e.m.f. coefficient up to α=320μV/K at *T=320.*

The ionization of donor impurity by κT heat energy order in semiconductors leads to electron transfer in conductivity band or on the level of acceptor impurity [8].

From the figure of work [9] it is seen that the mobility of charge carrier decreases with concentration increase of impurity of acceptors (N_a) and holes (N_d) in crystal.

In Mott work it is shown that the metallic drops can form at big concentration of electrons and holes in semiconductors and as a result of their interaction [8,10]. The impurity diffusion under action of thermal fields leads to formation of current filament, layer shunting and conduction decrease.

The maximum values of electric conductivity (σ), thermo-e.m.f. coefficient (α) electronic thermal conductivity ($\chi_э$) and power ($\alpha^2\sigma$) are achieved at temperature 300K for $Bi_2Te_{2,7}Se_{0,3}$. The doping by donor-nickel is carried out for the compensation of acceptor concentration. The thermo-e.m.f. coefficient increases with the increase of nickel concentration in the samples.

The nickel impurity 0,383 mass % when from layer surface form the coalescences of big sizes up to 600nm of $Ni_{1,297}Te$ composition, is the optimal concentration. The high mobility of charge carriers with optimal conductivity σ=1200Om^{-1}cm^{-1} and high coefficient of thermo-e.m.f. (Zeebek coefficient) α=320μV/K keep in the samples.

The thermoelectric properties α σ, $\chi_э$ at 300K are investigated. Thermal electronic conductivity is $\chi_э=L\sigma T$, [11] where $L=A(k_0/e)^2$. Coefficient A is defined by its dependence from the thermo-e.m.f. coefficient for the case of scatterimg elastic mechanism *(r=0,5).*Thermal electronic conductivity $\chi_э$ increases propertionally to conductivity σ. Taking under consideration the fact that thermal conductivity decrease in thermo-electrics leads to increase of efficiency, the obtaining of the doped samples by intercalation methods which gives the possibility to control the thermal electric conductivity $\chi_э$ is possible.

The doping of solid solution $Bi_2Te_{2,7}Se_{0,3}$ by nickel allows us to obtain the samples with high concentration of carriers by n-type conductivity in the aim of material embedding with *ZT* high quality factor.

CONCLUSION

Ni-Se-Te chains form in layers of sample intercalated by $Bi_2Te_{2,7}Se_{0,3}$ nickel ions. $Ni_{1,297}Te$ grains which significantly decrease electric conductivity that is connected with layer shunting form in Van-der-Wals spaces. The doped sample keeps the *n*-type conductivity.

It is established that the most optimal concentration is the nickel impurity in crystal $Bi_2Te_{2,7}Se_{0,3}$ 0,383 mass % that allows us to keep the high mobility of charge carriers at conductivity value σ=1200Om^{-1}cm^{-1} and also to support the high thermo-e.m.f. coefficient in region α= *320μV/K.*

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