EFFECT OF NANOISLANDS AND NANOWIRES ON THE THERMOELECTRIC QUALITY OF *Bi₂Te₃<Ni>* AND *Bi₂Te₃<Zn>*

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Work has been carried out to create materials with a vacuum gap of ~ (1-2) nm between nanograins to implement the tunneling mechanism of increasing the thermoelectric figure of merit and the corresponding elimination of phonon thermal conductivity. The formation of nanowires on the *(0001)* surface of Bi_2Te_3 crystals with impurities of easily diffusing *Ni* and *Zn* atoms has been studied. It is shown that the migration of atoms, the movement and coagulation of clusters form structures with nanoislands, on the basis of which nanowires are self-organized. Nanostructures in the form of islands, nanowires in the interlayer space are one of the reasons for the increase in the thermoelectric figure of merit in materials of the $A_2^VB_3^{VI}$ type.

Keywords: layered crystal, nanoislands, nanowires, thermoelectric figure of merit.
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INTRODUCTION

Layered crystals of the $A_2^VB_3^{VI}$ type are known as materials widely used in thermoelectricity. The topologically protected states discovered in them turned them into an intensively studied object, separated into a new type of condensed state of matter - a topological insulator. The prospect of increasing the thermoelectric figure of merit of these materials becomes more accessible when the technology uses the effects of self-organization of nanostructures, which play a special role in obtaining low-dimensional systems in them, such as nanosized islands and wires, moreover, wires and ridges of bands on the surface can be used as one-dimensional charge transfer channels with reduced dissipation. The presence of folds and stripes, miniature "ridges" on the surface of the Bi_2Te_3 topological insulator effectively modulates the Dirac electrons [1] so that they follow a path exactly corresponding to the topography of the crystal surface.

A certain type of impurities, without radically affecting the chemical and electronic structure of the layers, are ejected into the interlayer space and defective cavities, where they form nanostructures of various dimensions and shapes, they line up in a plane, wires or islands that can be used to control the interlayer distance. Charge transfer along *1D* wires, *2D* planes, and tunneling through nanoislands has the properties of a Luttinger liquid [2, 3], as well as the edge states of the quantum spin Hall effect induced by two-dimensional electronic states formed when the layers move apart, while transport in the bulk of the layers has the character of a Fermi liquid. We have previously reported [4–7] on the formation of such interlayer nanostructures and their effect on kinetic parameters as two-dimensional impurity layers forming superlattices and one-dimensional charge flow channels.

METHODS AND EXPERIMENT

The processes of formation of interlayer nanowires were studied by lining up clusters on the (0001) surface of a layered Bi_2Te_3 crystal doped with *Ni* and *Zn*.

AFM images were obtained on a Solver Next brand scanning probe microscope. X-ray diffraction studies of the *(0001)* surface were carried out on a Philips Panalytical X'Pert Pro XRD diffractometer.

The AFM images show an array of nanoislands arranged into one-dimensional structures. Diffusion processes lead to the approach of individual small nanoparticles and the formation of contacts between them, in the *(0001)* Bi_2Te_3 plane, where ordered nanoislands similar to quantum dots are formed.

Nickel and zinc have a small ionic radius; therefore, these atoms easily diffuse into the interlayer space and defective cavities of bismuth and antimony chalcogenides. Figures 1 and 2 show photographs taken with a scanning probe microscope: a) an array of individual nanoislands; b) nanoislands forming nanowires; profilogram showing the height and width of the nanowires;

c) X-ray diffraction pattern of a freshly cleaved Bi_2Te_3 *<Ni>* surface. Figure 1(c) shows *Ni*, $NiTe_2$, *NiTe* on the interlayer fresh cleaved surface of Bi_2Te_3 *<Ni>*. Migration and interaction of clusters with each other leads to the formation of filaments in the framework of a process that has a "bottom-up" direction. The main reason for the formation of stressed islands on the surface is the relaxation of elastic stresses at the edges of the layers and the interaction of the islands through the stresses they create in the crystal. The shape of islands can change significantly during overgrowth or post-growth annealing. Figure 1a shows the final result of the dynamics of the formation of large islands from small and linear formations formed from them, which can be called nanowires.

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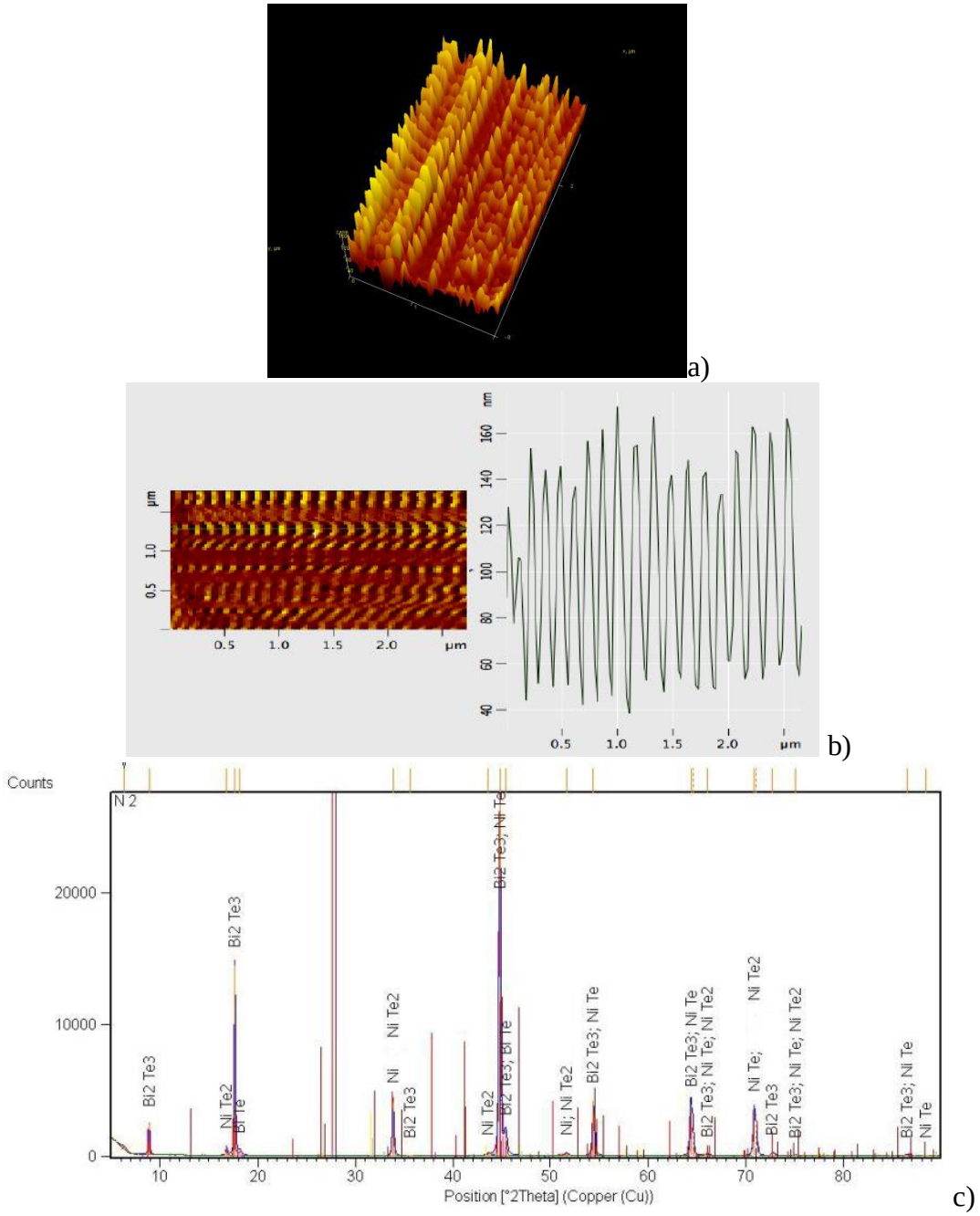

Fig.1. 3D AFM image (nanoislands and nanowires) of Bi_2Te_3<Ni> - a); 2D AFM image of Bi_2Te_3<Ni> cross section profilograms - b); Bi_2Te_3<Ni> X-Ray diffraction pattern - c).

The dynamics of the formation of nanofragments is such that nanoislands similar to QDs initially appear, and later, in the course of evolution, the islands can merge, forming bridges with the preservation of their shapes and heights. As a result of the developed technology, an ordered array of nanoislands was formed in the process of self-organization on the (0001) plane. Particle aggregation leads to a decrease in the distribution density and the appearance of large nanoobjects. Electron microscopic images showed that nanoobjects are formed from nanoislands in the process of diffusion at temperatures of 500-600K. Penetrating mainly into the interlayer space, impurities create three-dimensional periodic structures consisting of arrays of points between the layers of quintets, which, as a result, move apart. The enhancement of anisotropy during the self-organization of nanoislands leads to an increase in the role of "bending" vibrations in the thermal properties of the crystal. The role of this specific branch of acoustic oscillations and its behavior in layered crystals according to the Lifshitz theory [8] was reported in [9]. The "bending" branch corresponds to oscillations propagating in the plane of the layers with atomic displacements in the direction perpendicular to the layers and makes the main contribution to heat transfer, with a temperature dependence that has three different characters and the greater the anisotropy of the crystal, the more significant its role in the "membrane" effect (increase in frequencies " bending

"vibrations during stretching of the layers), leading to negative thermal expansion in the plane of the layers. The anomalies of the kinetic parameters observed by us occurred in the region of a linear temperature increase in the heat capacity, where the contribution of the "bending" branch dominates [9]. Scattering of this phonon branch at the base of the islands, which are chemically bound to quintets, leads to thermalization of the QD levels followed by tunneling. This region, where the heat capacity is $C \sim T^2$, and the temperature increase in the thermal conductivity $\chi \sim T^{2+X}$ (where x can be determined by tunneling processes, i.e., the size and density of the islands), is marked as a region of thermal anomaly. Note that the decrease in the lattice thermal conductivity of quintet layers in this region can be somewhat compensated by an increase in the thermal conductivity of the Luttinger liquid of the tunneling current in the nanowires. The thermoelectric efficiency of these samples is higher than that of undoped ones, apparently due to a decrease in the total thermal conductivity of the "quintet layers- nanowires " composite by an increase in the role of phonon scattering of layers at the boundaries of nanowires. These processes are dominated by phonons corresponding to bending vibrations, which have a quadratic dispersion form. Aggregated structures connected to each other by a chain of clusters provide charge tunneling along conducting channels, with the main contribution being made by several highly conductive channels. Since the radius of charge localization on nanoislands is smaller than the distance between localized states in these structures, charge transfer occurs via tunnel hops. Differences in size and another type of inhomogeneity lead to a scatter of energy levels corresponding to different localized states, so the transitions of charge carriers between localization centers are accompanied by absorption or emission of phonons. Since the distance between the centers does not allow the transfer of phonons, the phonon component of the thermal conductivity decreases accordingly. In addition, the mechanism of broadening the interlayer space is triggered, which hinders the transfer of vibrational energy between layers - phonon confinement, which also leads to a decrease in phonon thermal conductivity.

Clusters forming nanowires broaden the van der Waals space without destroying the topologically protected states [10] and shift them into the inner quintet [11]. At the temperatures of existence of non-dissipative transport over topologically protected states, the probability of an increase in thermoelectric power increases [12]. The choice of the temperature regime for annealing the doped crystals made it possible to obtain interlayer nanostructures of the required dimension and height. It was found that the migration and diffusion aggregation of atoms leads to coagulation of a one-dimensional series of clusters, while the relaxation of elastic stresses on defect centers and the interaction of clusters lead to the formation of nanowires. This is also evidenced by AFM images in Bi_2Te_3 <Zn>, on the Fig. 2-4 nanostructures are shown in different directions by lines.

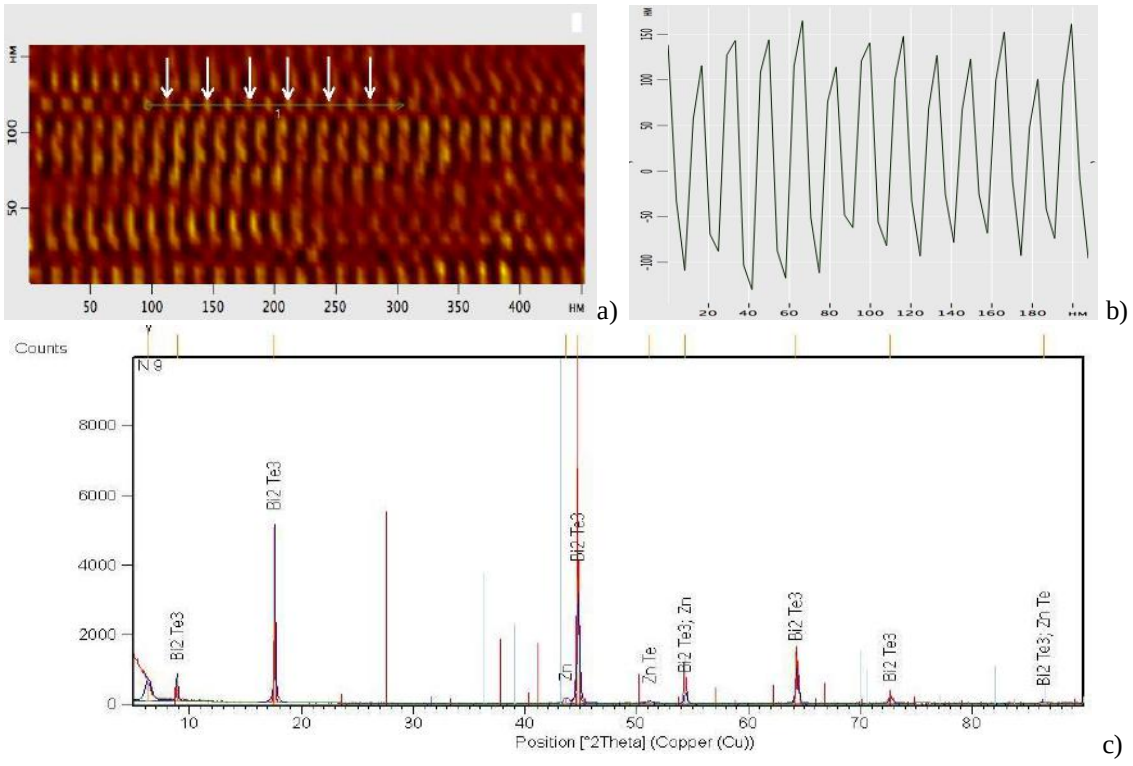

Fig.2. *2D* AFM image of the *(0001)* Bi_2Te_3 <Zn> surface – a); profilogram along the line shown in Fig. 2a – b); Bi_2Te_3<Zn> X-Ray diffraction pattern - c).

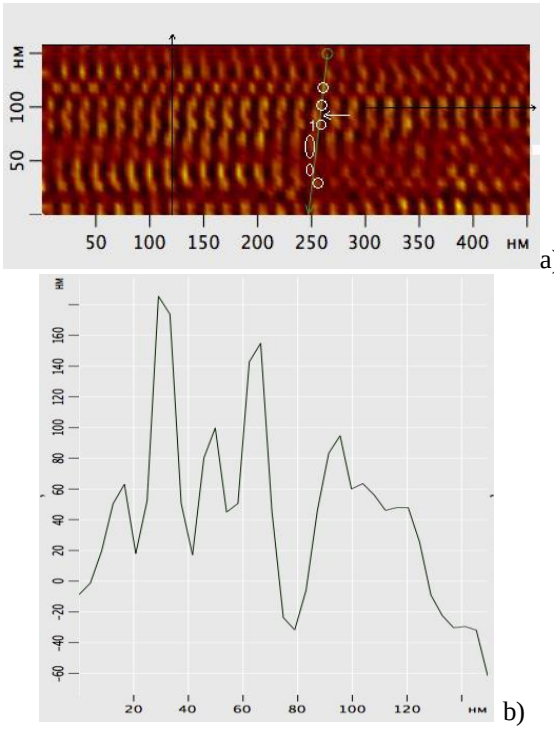

Fig.3. 2D AFM image of (0001) Bi_2Te_3 <Zn> - a); profilogram along the line shown in Fig. 3a – b)

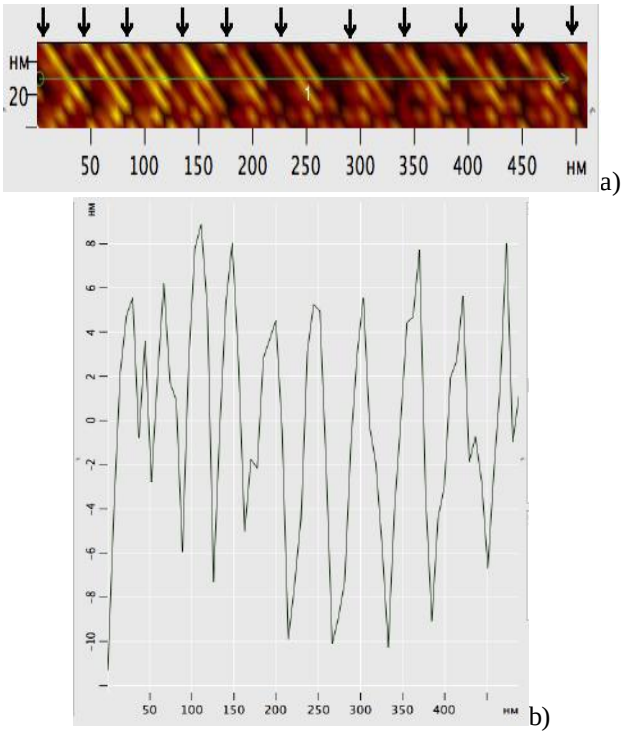

Fig.4. 2D AFM image of the *(0001) Bi_2Te_3<Zn>* - a); profilogram along the line shown in Fig. 4a – b)

Fig. 2a shows a *2D* AFM image of the *(0001) Bi_2Te_3<Zn>* surface, small nanoparticles are indicated by white arrows, and Fig. 2b shows a profilogram (along the line shown in Fig. 2a). It can be seen from this profilogram that the interlayer contacts are located approximately at distances of 10–15 nm from each other. Figure 2(c) shows *Zn* and *ZnTe* on the interlayer fresh cleaved surface of *Bi_2Te_3<Zn>*. Figure 3(a, b) shows a *2D* AFM image with a profilogram across the section (Fig.3a), nanoobjects are marked with white circles in Fig.3a. The profilogram given in Fig.2b shows that the length of the nanowires is nonuniform in the transverse direction; point contacts with sizes of the order of ~ 15–20 nm are also formed between them. A fragment of these nanowires is shown in Figs.4a,b (they are marked with black arrows in Fig. 4a), it can be seen from the profilogram that point contacts are formed at distances of ~20–30 nm. Three

mechanisms can be named that contribute to an increase in the thermoelectric figure of merit when using nanostructures [13-17]: additional scattering of phonons at the boundaries of nanograins; electron tunneling between nanostructural elements; energy filtering of carriers due to the presence of potential barriers between nanograins. The paper [13] discusses these mechanisms of increasing the quality factor.

The focus is on the effect of nanograin sizes on the value of kinetic coefficients in solid solutions based on p–$Bi_xSb_{2-x}Te_3$ (x=0.3÷0.4) obtained by mechanical activation treatment followed by hot pressing. *Electron tunneling.* To study the influence of tunneling of current carriers on the thermoelectric figure of merit in bulk nanostructured samples, the shape of crystalline nanograins was modeled as a pair of truncated cones with a common base, and these grains were separated by tunneling barriers [18]. When calculating the heat flux through the tunnel gap, the mismatch between the electron and phonon temperatures was taken into account. The tunneling probability for the case of bismuth telluride was calculated exactly. The thermopower, electrical conductivity, and Lorentz number for the tunnel barrier were calculated [18]. Then, the heat flux and effective kinetic coefficients in nanograins were calculated. To study the temperature distribution of electrons and phonons, we used the electron and phonon energy balance equations and also the continuity equation for the electric current. *Additional phonon scattering.* When calculating the lattice thermal conductivity in the Debye model [19], we took into account phonon–phonon scattering, phonon scattering by impurities and isotopes, and also at nanograin boundaries. Calculations have shown that the scattering of phonons at the boundaries of nanograins with sizes of ~ (10-20) nm in bulk nanostructures based on the Bi_2Te_3 solid solution can reduce the lattice thermal conductivity by (20-30) % compared to the initial material. *Energy filtering of charge carriers.* The presence of potential barriers between different elements of the nanostructure can lead to a strong energy dependence of the mean free path of carriers near the chemical potential level. Then, energy filtering can occur [13, 20, 21], i.e., carriers with energies above the Fermi energy will overcome the boundary between nanograins, practically without scattering. The table compares the various mechanisms for increasing the quality factor (Z).

Z increase mechanism	Implementation conditions	Possible Z increase
Additional phonon scattering	L<(10-20) nm	(15-25)%
Tunneling of charge carriers	L<(10-20) nm vacuum gap between nano grains ~(1-2)nm	ZT up to 3,0 -3,5
Energy filtering of charge carriers	L<(20-30) nm The decrease in the electrical and thermal conductivity of the lattice is compensated	(20-40)%

It can be seen from the table that for the implementation of all three mechanisms for increasing the quality factor, small sizes of nanograins ~ (10–20) nm are required. Technologically, it is quite difficult to create such a nanostructure; the reason is the increase in the size of the initial nanoparticles due to recrystallization. Thanks to this process, grain sizes exceed 100 nm. Some reduction in grain size (2–3 times) can be achieved in nanocomposites when nanoinclusions with a layered structure are added to the initial matrix [17], but the grain size still cannot reach the required value L<(10–20) nm. The creation of a vacuum gap of ~ (1-2) nm between grains for the implementation of the tunneling mechanism of increasing the quality factor and the corresponding elimination of phonon thermal conductivity is unlikely to be achieved by mechanical activation treatment followed by hot pressing. In addition, the study by electron microscopy did not reveal any gaps between nanograins, neither vacuum nor oxide [15-17, 19]. However, the quantum point contacts we discovered (see Fig. 2-4) eliminate these problems; conditions arise for the realization of additional scattering of phonons at L<20 nm.

CONCLUSION

The implementation of all the mechanisms listed in the table for increasing the quality factor in a nanothermoelectric based on a Bi_2Te_3 solid solution could lead to an increase in ZT to 3.5 at room temperature. If vacuum gaps between grains ~ (1-2) nm cannot be created, but if a bulk nanostructure with grain sizes ~ (10-20) nm is created, we can expect an increase in ZT to 1.5. We have so far implemented the conditions under which ZT reaches 1.1.

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