

IMPURITY TYPE INFLUENCE ON SHAPE OF INTERLAYER NANOSTRUCTURES IN BISMUTH CHALCOGENIDES

**K.Sh. GAHRAMANOV¹, S.Sh. GAHRAMANOV¹, Kh.V. ALIQLIYEVA^{1,2},
Z.I. BADALOVA¹ N.A. ABDULLAYEV^{1,3}**

¹*Institute of Physics after name G.M. Abdullayev of ANAS, H. Javid ave.131,
AZ1143 Baku, Azerbaijan*

²*Sumgait State University, 43th district, Baku str., 1, AZ5008 Sumgait, Azerbaijan*

³*Baku State University, Z. Xalilov str., 33, AZ1148 Baku, Azerbaijan*

e-mail: samir.gahramanov@gmail.com

Materials with arrays of nanoislands of various sizes and distribution densities have been obtained. The formation mechanism of the above nanostructures is described, which is associated with migration, coalescence, and clustering in the interlayer space of impurity not dissolved in the layers and a superstoichiometric excess.

INTRODUCTION

In the nanometer range, many properties of a substance change and new opportunities open up in materials science and technology. One of the ways to increase the thermoelectric figure of merit of layered crystals of the $A^V_2B^{VI}_3$ type is through a decrease in the phonon component of thermal conductivity and an increase in the value of the thermo-EMF coefficient. with an increase in the density of states near the Fermi level is the use of spatially inhomogeneous materials and nanostructures, the dimensions of which are comparable with the characteristic wavelengths of electrons (10-50 nm) and phonons (1 nm). For example, nanostructures self-organizing in the van der Waals space between the layers of crystal sandwiches and defective cavities of layered crystals of bismuth and antimony chalcogenides effectively scatter and limit the propagation of phonon modes, but at the same time, the transformation of a part of the transfer into a hopping form reduces the mobility of charge carriers. To increase the thermoelectric figure of merit, it is required to choose a regime with limited phonon propagation with simultaneous effective charge transfer and solve the problem of predictable self-organization - grouping of atoms in a certain way, in order to eventually obtain materials with optimal properties.

Such materials, with the ability to control the interlayer distance, as well as the shapes and sizes of nanoislands on the surface formed during crystal splitting, can be freely used for spin-oriented transfer as topological insulators. In [1], one-dimensional defects were considered as quantum-mechanical elements, and it was noted that a topological insulator is resistant to order violations with non-propagating dislocations, and this is a manifestation of a quantum phenomenon. It was shown in [2] that topologically protected states are not destroyed in the presence of quantum dots on the surface, they are not captured by the surface, and this is confirmed by the predominance of small-angle scattering and the suppression of backscattering processes. This opinion is consistent with a number of works showing the stability and

inviolability of the topological state on surfaces with defects, bond breaks, and steps [3,4]. In [5], a model was proposed for controlling non-dissipative quantum transfer channels by controlling mixing and interference of edge state wave functions using transitions in quantum dots on the surface of a magnetic topological insulator, with the possibility of increasing operating temperatures in corresponding applications.

To understand the thermodynamics of nanoparticles and its dependence on particle size, there are various approaches, such as classical thermodynamic calculations, molecular dynamics simulations, and ab initio calculations. The atomistic approach, based either on molecular dynamics simulations or ab initio calculations, usually leads to inconsistent results, often due to inaccurate particle size determination, and a more realistic particle size determination is possible through a detailed analysis of the electronic structure obtained from first-principles calculations. [6] shows difficulties in determining the dependence of surface energy on nanoparticle size, [7] also shows a slight dependence of surface energy on particle size, and it is recommended to use surface energy values only for equivalent bulk materials if detailed data for nanoparticles are not available. In [8], a bond-oriented model was proposed that is capable of estimating the cohesive energy in the range of monometallic and bimetallic nanoparticles and the tendency of behavior during mixing of nanoalloys, which is in good agreement with calculations based on the density functional theory. This model uses data on the energy of diatomic bonds and bulk energy of cohesion and structural information about nanoparticles and is used to calculate the energy of nanoparticles of any morphology and chemical composition. The preservation of thermodynamic concepts and the use of thermodynamic parameters of nanoparticles, along with the rejection of parameters that are not suitable for small systems, will make it possible to understand the features of the transition from macro to nano systems [9].

In this work, estimates of the structural ordering of nanoformations are based on experimental and empirical data. Dimensions and shapes, distribution density, as well as the composition of nanostructures affect the electrical characteristics of the material. The purpose of this work was to study the self-organization of interlayer nanostructures of bismuth chalcogenide crystals using impurities and various technological modes.

GROUPING OF NANOPARTICLES

Nanoscale structures and dislocation centers play a quantum mechanical role in the localization and transfer of charge and heat. The formation of these structures is associated with mass transfer and plastic deformation, which has the nature and regularities inherent in the organization of similar structures in other solid materials. As is known, in many layered crystals, the effect of expulsion of excess stoichiometry and impurities from the layers that form crystal blocks into the interlayer van der Waals space takes place; this self-purification is called the self-intercalation effect [10]. The results of [11] demonstrated that the self-purification phenomenon depends on the size of the impurity elements, the

distance separating them, as well as on interlayer van der Waals interactions, and a theoretical model is presented showing how each of these key factors contributes to the self-purification phenomenon. In this context, of interest are layered systems whose van der Waals spaces can serve as nanoreactors [12–14] for the formation of various nanofragments. The surface has a structuring effect on the formation and growth of nanoparticles. Self-organization of nanosized structures on the surface of the interlayer space leads to the formation of elements that depend in shape on the composition and amount of impurities and the temperature regime of diffusion and annealing. Building an array of nanoislands on the (0001) crystal surface is interesting from the point of view of controlling the material properties. The proposed ways of diffusion of particles and their aggregation are associated with the process of filling with impurities the places around the nodes of dislocation networks and vacant nodes, which can be considered telluride (selenium) vacancies, on the van der Waals surface (0001). Due to the active interaction during annealing, atoms accumulate around them, forming nano-objects (Fig. 1.), including interlayer nanostructural elements (INSE).

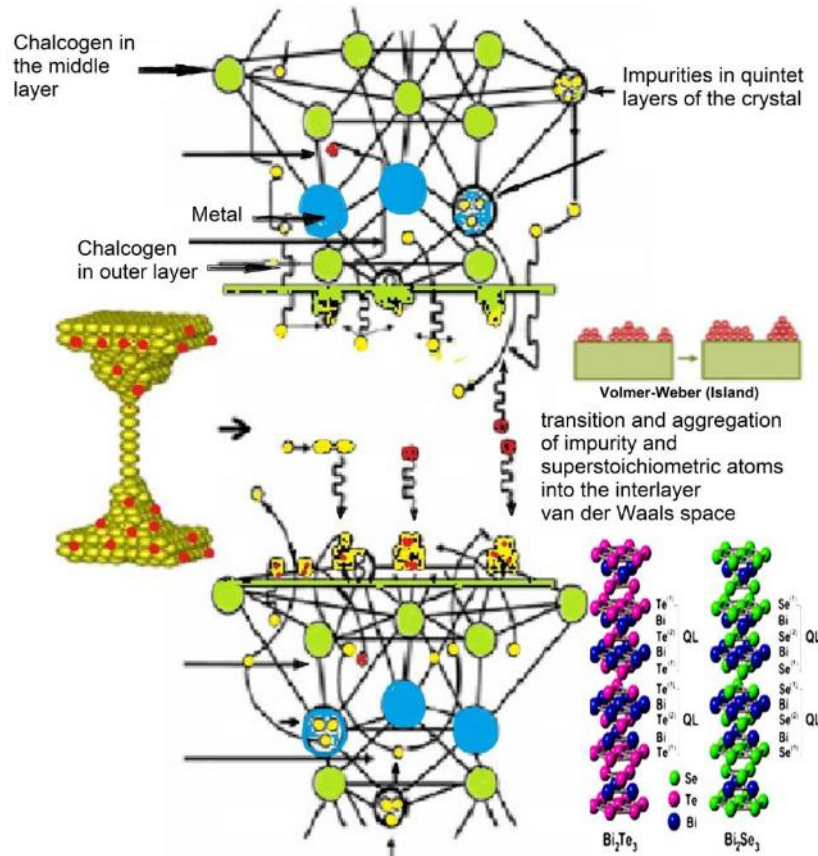


Fig.1. Along the layers between opposite sides of the lattice in the $Te(Se)^{II}-Te(Se)^{II}$ space, superstoichiometric atoms and impurities in the process of self-purification and coalescence are formed into nanoislands by the Volmer-Weber mechanism.

An increase in temperature after the onset of crystallization leads to segregation and coalescence of nanoparticles, which is used in the technology of

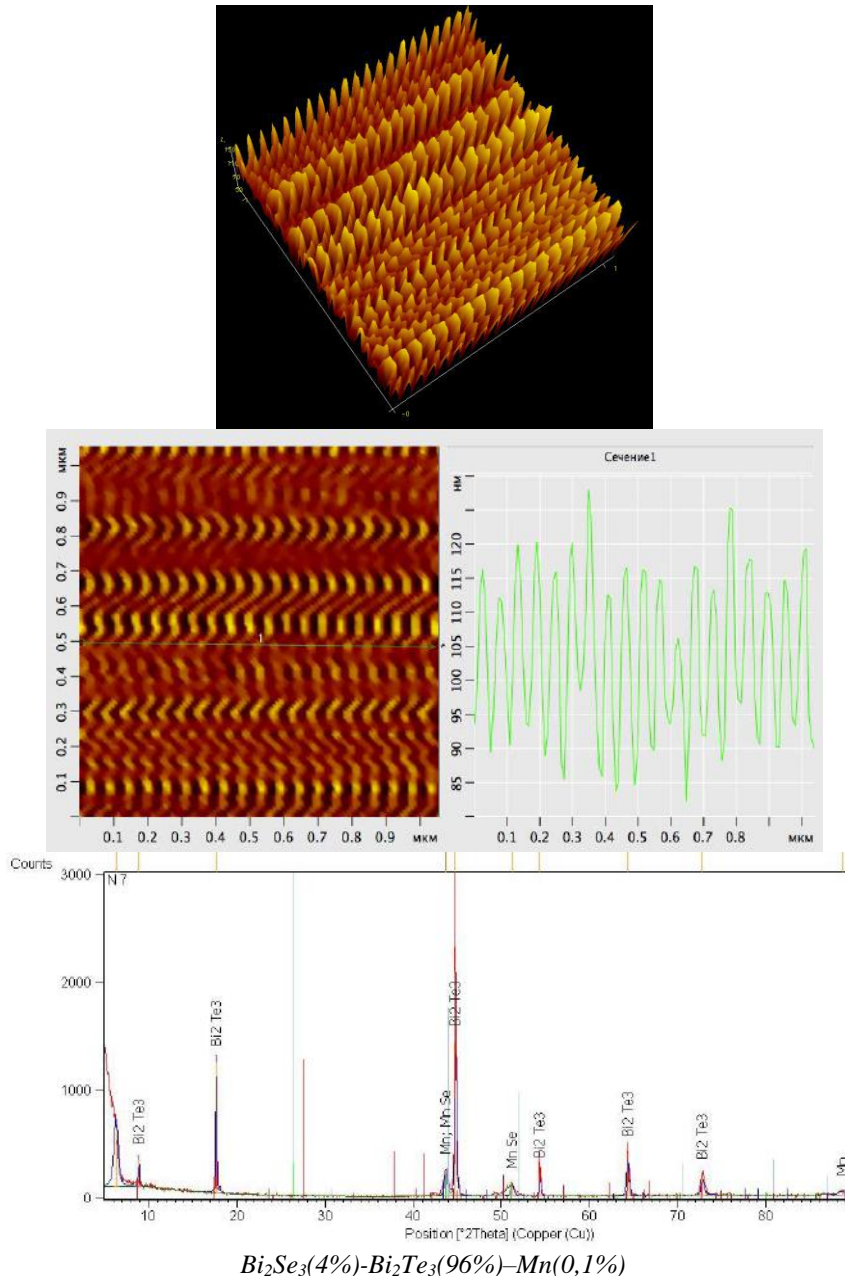
obtaining multicomponent nanoparticles [15]. Under certain temperature regimes, the stress in the layer is unfavorable for two-dimensional growth, and a

spontaneous transition to three-dimensional island growth occurs. In the process of island growth, they influence each other, and as a result, an array of islands is formed, ordered by size, and, under certain conditions, by mutual arrangement. Apparently, the largest INSE can aggregate into cavities ending in edge dislocations and containing other large layer defects, where elastic stresses are strongest. The driving force behind the formation of three-dimensional islands is bulk elastic relaxation, i.e. a decrease in the elastic energy during the formation of islands compared to the elastic energy of the stressed layer of inclusions in the interlayer space and is very similar to the Volmer-Weber mechanism. When a crystal is cleaved, it is precisely such crotches that are opened in the first place, where INSE are observed. The aggregation of impurity and superstoichiometric inclusions into these spaces should reduce the crystal energy and elastic stresses. The paths of penetration of elements from the volume of quintets into van der

Waals and defect gaps can run along screw dislocations. Presumably, they are concentrated at the ends of screw dislocations and other defect centers, eventually creating conical protrusions and nanoislands in the interlayer space, since the rest of the van der Waals surface is chemically inert, and open valence (dangling) bonds appear on screw dislocations and vacancies.

EXPERIMENTAL RESULTS

Diffusion processes in the direction of the base surface (0001) not only form individual nanostructural elements, but also connect them in a continuous chain, forming charge flow channels. On the van der Waals surface, which has the largest "gap" $Te(Se)^{II}-Te(Se)^{II}$, arrays of nanoislands are placed, forming bound structures consisting of individual INSE (Fig. 2.), and connected with each other in a continuous chain.



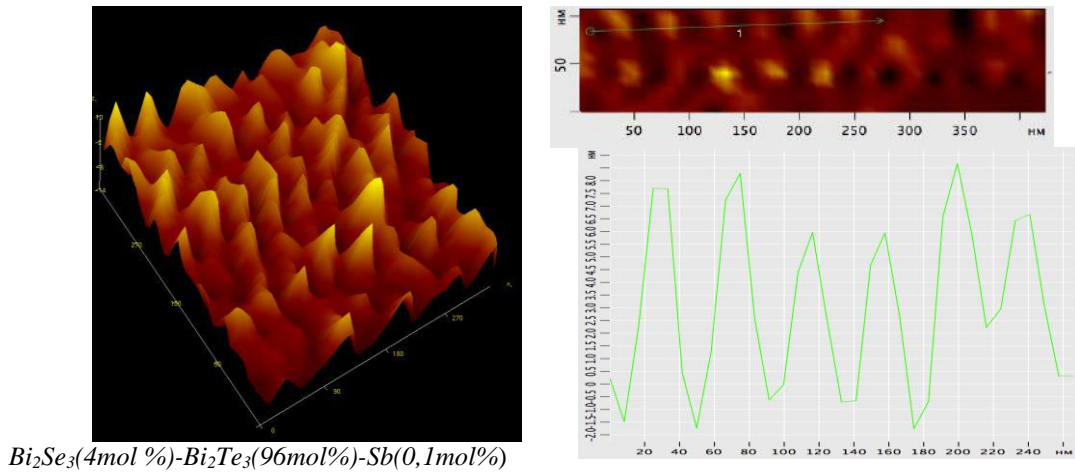


Fig. 2. The end result of the dynamics of the formation of large islands from small islands and linear formations formed from interlayer nanostructural elements is demonstrated. 3D and 2D AFM images, a profile along the cut line in the 2D AFM image and an X-ray diffraction pattern of the corresponding surface for

Bi_2Se_3 (4mol%) - Bi_2Te_3 (96mol%) - Mn (0,1mol%) and Bi_2Se_3 (4mol%) - Bi_2Te_3 (96mol%) - Sb (0,1mol%). The influence of the surface topography on the percolation threshold, which leads to changes in the transfer parameters, is determined by the distribution density of nanoislands. If a particle reaches the $Te(Se)^{(1)}$ boundary, then it is either reflected from it or deposited in telluride-selenium vacancies and at the nodes of the dislocation network. It is assumed that a particle moving in space, in contact with a cluster or nanoisland, sticks to it with a certain probability. At certain stages, nanoislands grow perpendicular to the (0001) plane, which is clearly seen from the 3D AFM images (Figs. 2-8). The process of coagulation in the $Te(Se)^{(1)}$ - $Te(Se)^{(1)}$ space reaches its peak, at which INSEs in contact with each other are combined into a single fractal surface above the percolation threshold. If the density of nanoislands several nanometers in size is greater than the corresponding percolation threshold, then conduction in them occurs through one-dimensional channels by the diffusion mechanism. Below the percolation threshold, nanostructures are dominated by hopping conduction due to electron tunneling through the barriers separating them. The transition from hopping to diffusion transport is observed with a change in the density of nanoislands and the degree of their filling with charge carriers. During overgrowth or post-growth annealing, their shapes can change significantly. The main part of nanoislands is cone-shaped nanoparticles. It can be seen that there are nanoislands of different areas; they can be characterized by their base area, volume, and height relative to the particle boundary. Depending on the impurity used, the islands have: height from 2 nm to 80 nm; area 1200 nm² - 40000 nm²; volume from 400 nm³ to 0.1 cm³.

Electron microscopic images showed that nano-objects are formed in the process of diffusion at temperatures above 500K. Penetrating mainly into the

interlayer space, impurities create bulk periodic superstructures consisting of arrays of nanoislands between layers of quintets (period from 200 to 1000 quintets), which, as a result, move apart and enhance the anisotropy of the crystal. This, in turn, leads to an increase in the role of "bending" oscillations in the thermal properties of the crystal. The role of this specific branch of acoustic vibrations and its behavior in layered crystals according to the Lifshitz theory [16] was reported in [17]. The "bending" branch corresponds to vibrations propagating in the plane of the layers, with displacements of atoms in the direction perpendicular to the layers, and makes the main contribution to heat transfer, with a temperature dependence that has three different patterns. The greater the anisotropy of the crystal, the greater its role in the "membrane" effect (increase in the frequencies of "bending" vibrations when the layers are stretched), leading to negative thermal expansion in the plane of the layers. Scattering of this phonon branch at the base of the INSE, which are chemically coupled to quintets, leads to level thermalization followed by tunneling. This region, where the heat capacity is $C \sim T^2$, and the temperature increase in the thermal conductivity coefficient $\chi \sim T^{2+X}$ (where X can be determined by tunneling processes, i.e., the size and distribution density of the INSE), is marked as a region of thermal anomaly. Note that the decrease in the lattice thermal conductivity in this region can be somewhat compensated by an increase in the thermal conductivity of the tunneling current. The thermoelectric efficiency of these samples is higher than ~15% than that of undoped ones, apparently due to a decrease in the total thermal conductivity of the "quintet layers - INFE" composite, an increase in the role of layer phonon scattering at the boundaries of the separated layers and INSE faces. These processes are dominated by phonons corresponding to bending vibrations, which have a quadratic dispersion form.

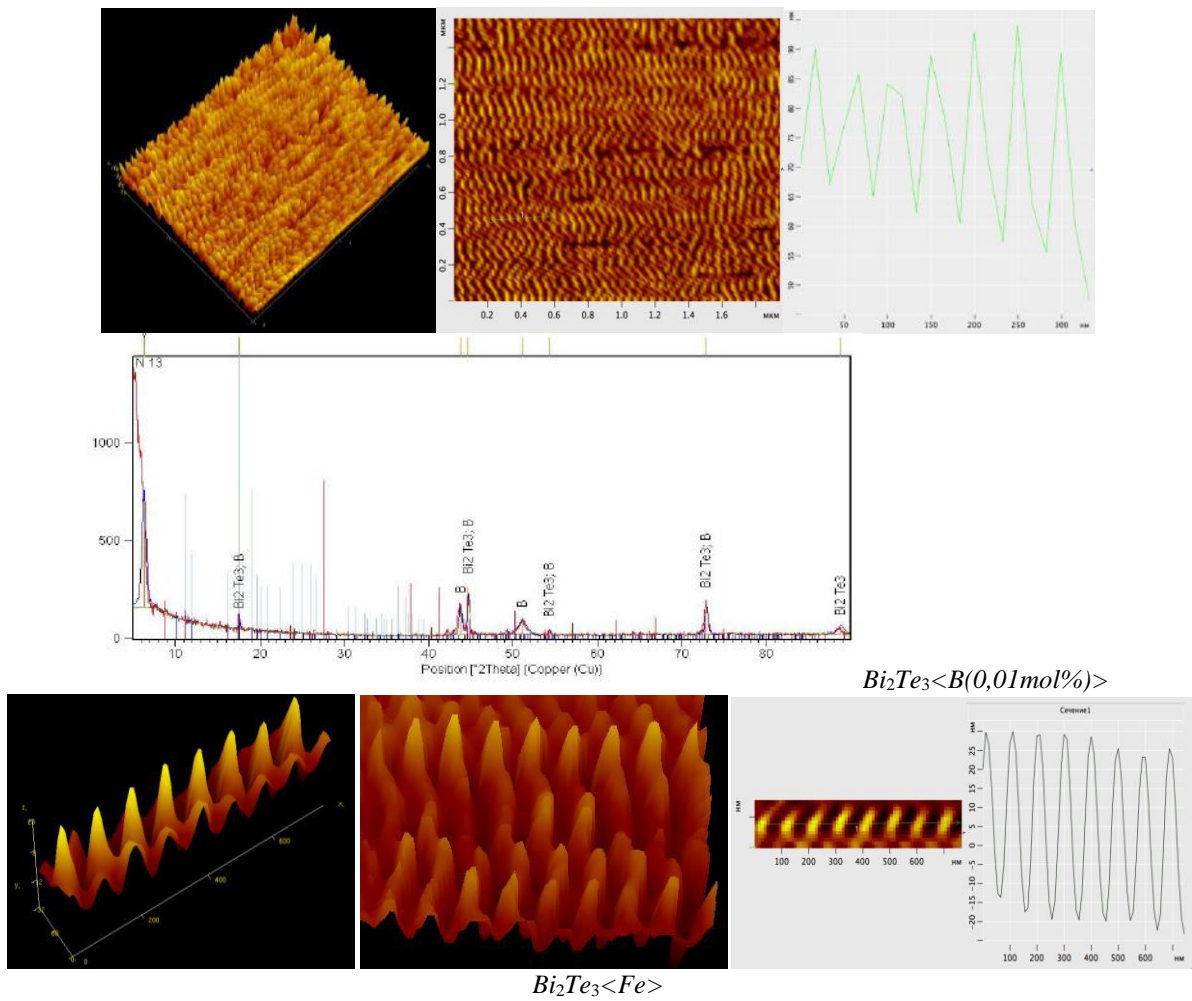


Fig. 5. 3D and 2D AFM images, 2D AFM slice line profilogram and X-ray diffraction pattern of $\text{Bi}_2\text{Te}_3\langle\text{B}(0,01\text{mol}\%)\rangle$ and $\text{Bi}_2\text{Te}_3\langle\text{Fe}\rangle$ surfaces.

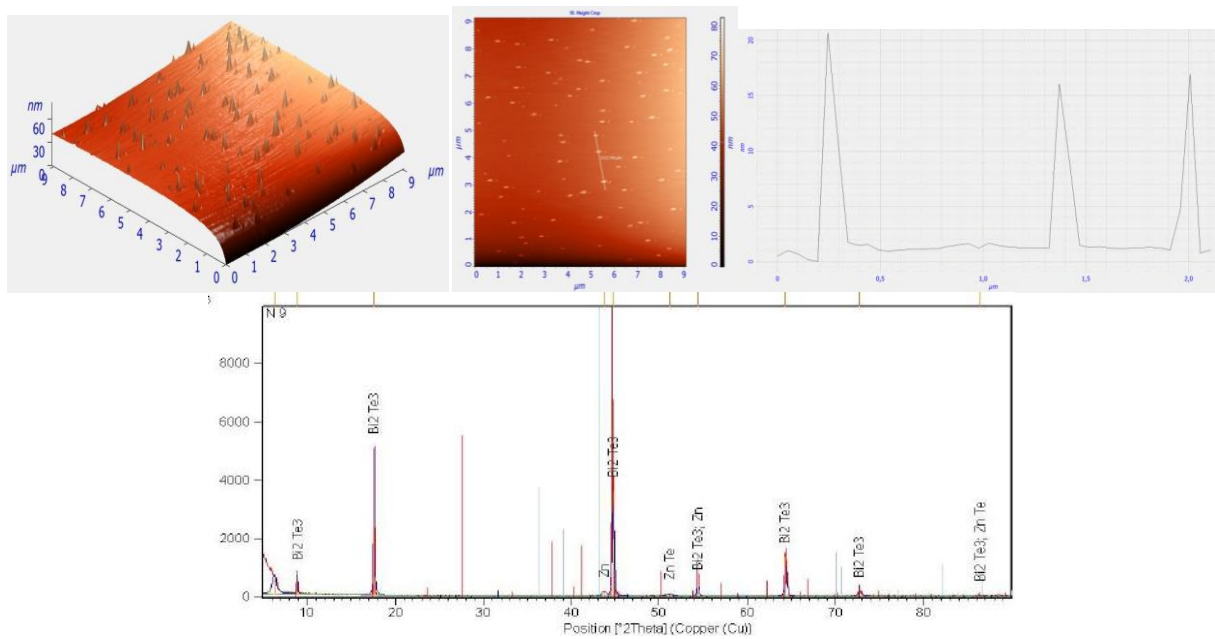


Fig. 6. 3D and 2D AFM images, 2D AFM slice line profilogram and X-ray diffraction pattern of the $\text{Bi}_2\text{Te}_3\langle\text{Zn}\rangle$ surface.

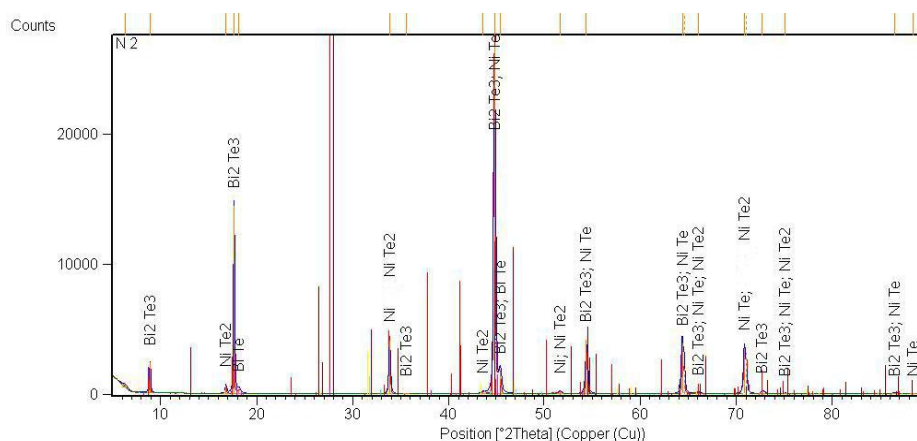


Fig. 8. 3D and 2D AFM images, 2D AFM slice line profilogram and X-ray diffraction pattern of the $Bi_2Te_3<Ni>$ surface.

The difference between the components in nanostructures is a parameter that affects their shape, and can also change the nature of segregation phenomena and affect the structural ordering. Thus, the choice of an impurity with a certain ratio of atomic radii, in combination with the regulation of the rate of temperature change, makes it possible to obtain

materials with various shapes and sizes of interlayer nanostructural elements.

This work was supported by the Foundation for Science Development at the President of the Azerbaijan Republic- grant № EIF/MQM/ Elm-Tehsil-1-2016-1(26)-71/16/1-M-01.

[1] Y. Ran, Y. Zhang, A. Vishwanath. Nature Phys., 5, 298–303 (2009). <https://doi.org/10.1038/nphys1220>

[2] A. Kundu, A. Zazunov, A. L. Yeyati, T. Martin, R. Egger. Phys. Rev. B 83, 125429 (2011). <https://doi.org/10.1103/PhysRevB.83.125429>

[3] Z. Alpichshev, J.G. Analytis, J.-H. Chu, I.R. Fisher, A. Kapitulnik. Phys. Rev. B, 84, 041104 (2011). <https://doi.org/10.1103/PhysRevB.84.041104>

[4] K. Kobayashi. Phys. Rev. B 84, 205424 (2011) <https://doi.org/10.1103/PhysRevB.84.205424>

[5] N. Varnava, J.H. Wilson, J.H. Pixley, D. Vanderbilt. Nat. Commun., 12:3998, (2021), <https://doi.org/10.1038/s41467-021-24276-5>

[6] B. Molleman, T. Hiemstra. Phys. Chem. Chem. Phys., (2018). 20(31), 20575– 20587. doi:10.1039/c8cp02346h

[7] D. Vollath, F.D. Fischer, D. Holec. Beilstein J. Nanotechnol. 2018, 9, 2265–2276. doi:10.3762/bjnano.9.211

[8] Z. Yan, M.G. Taylor, A. Mascarenno, G. Mourmpakis. Nano Lett., 2018, 18, 4, 2696–2704, doi:10.1021/acs.nanolett.8b00670

[9] C.Q. Sun. Size dependence of nanostructures: Impact of bond order deficiency. Progress in Solid State Chemistry. 35(2007) 1-159.

[10] C.Ш. Кахраманов. Неорг. матер., 2008, т.44, в.1, с. 17 -25.

[11] J.-S. Sun, J.-W. Jiang, H.S. Park, S. Zhang. Nanoscale, (2018). 10(1), 312–318. doi:10.1039/c7nr06553a

[12] Ф.К. Алескеров, С.Ш. Кахраманов. Металлофизика и новейшие технологии. 2008.т. 30, № 11,с. 1465-1477. Ф.К. Алескеров, С.Б. Багиров, С.Ш. Кахраманов, Г. Кавеи. Transact. Azerb.NAS:ser. phys.-math. tech. sci. Phys. Astronomy. 2010, №5, с.52-55.

[13] Б.М. Гольцман, В.А. Кудинов, И.А. Смирнов. Полупроводниковые термоэлектрические материалы на основе Bi_2Te_3 . М.: Наука, 1972. 319с.

[14] А.Ю. Колосов, N.Yu. Sdobnyakov, V.S. Myasnichenko, D.N. Sokolov. J. Synch. Investig.10,1292-1299(2016). doi.org/10.1134/S102745101605075X

[15] И.М. Лифшиц. ЖЭТФ. 1952. т. 22, в.4, с. 475 – 486.

[16] Н.А. Абдуллаев, Р.А. Сулейманов, М.А. Алджанов, Л.Н. Алиева. ФТТ. 2002, т.48, № 4, с.1775-1779.

**К.Ш. Кахраманов, С.Ш. Кахраманов, З.И. Бадалова,
Х.В. Алигулиева, Н.А. Абдуллаев**

**ВЛИЯНИЕ ВИДА ПРИМЕСИ НА ФОРМЫ МЕЖСЛОЕВЫХ НАНОСТРУКТУР В
ХАЛЬКОГЕНИДАХ ВИСМУТА.**

Получены материалы с массивами наностроекков, различных размеров и плотностей распределения. Описан механизм образования вышеперечисленных наноструктур, связанный с миграцией, коалесценцией и кластерированием в межслоевом пространстве не растворенной в слоях примеси и сверхстехиометрического избытка.

**К.Ş. Qəhrəmanov, S.Ş. Qəhrəmanov, Z.İ. Bədəlova,
H.V. Əliguliyeva, N.A. Abdullayev**

**BISMUT XALKOGENİDLƏRİNDƏ LAYLARARASI NANOSTRUKTURALARIN FORMASINA
AŞQAR NÖVLƏRİNİN TƏSİRİ**

Müxtəlif ölçülü və paylanma sıxlığı olan nanoadalar massivləri olan materiallar alınmışdır. Bu nanostrukturaların əmələ gəlmə mexanizmi təsvir edilmişdir ki, bu da laylarda həll olunmamış aşqarların və superstoixiometrik artıqların laylararası məkanında miqrasiyası, birləşməsi və klasterləşməsi ilə əlaqələndirilir.