National Technical University "Kharkov Polytechnic Institute",
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Department of Theoretical & Experimental Physics

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Department of Theoretical & Experimental Physics

Laboratory of Semiconductor Physics and Thermoelectric Materials Science

Head of the Laboratory - Elena Rogacheva

Professor, D.Sc. in Physics and Mathematics

Research areas :

1) ***Physics of Phases of Variable Composition (solid solutions and non-stoichiometric compounds)***

2) ***Classical and Quantum Size Effects in Semiconductor and Semimetal Nanostructures***

3) ***Low-Dimensional and Bulk Materials for Thermoelectric Energy Conversion***

4) ***Structure and Transport properties of Topological Insulator Thin Films***

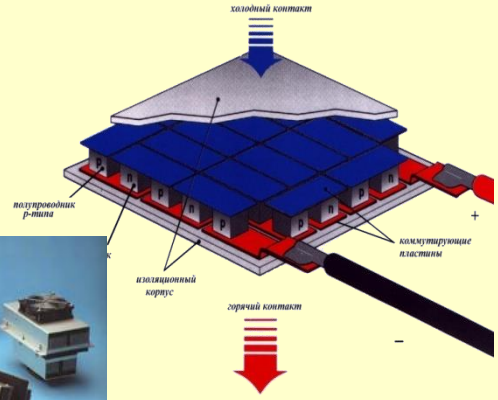
Thermoelectric energy converters

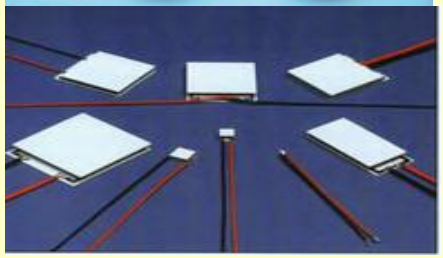
The main objects ***of the studies are bulk materials and thin films based on IV-VI & V_2VI_3 semiconductor compounds and Bi–Sb semimetal solid solutions.***

All of them are the best thermo-electric materials

Thermoelectric generators and cooling devices present several advantages compared to other energy conversion technologies. The range of application of thermoelectric sources of energy is rather wide, from power supply of automatic weather stations to power supply of spacecrafts

Thermoelectric cooling has become one of the most important and promising directions of refrigerating engineering. (modern electronics, computer engineering, cryomedicine, agriculture, metrology, and private houses.





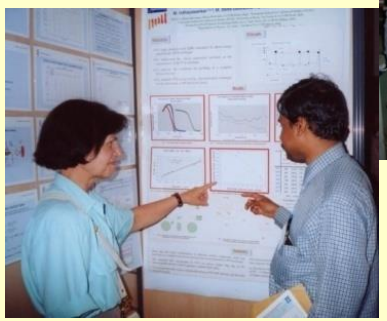
The recent developments in nanotech-nologies have led to the appearance of a new method of controlling the properties in thermoelectricity: changing the dimensions of a system.

About the Laboratory

Bulk and Nanomaterials for Thermoelectric Energy Converters

The goal of the research is to develop physical foundations for controlling thermo-electric properties of *low-dimensional nanostructures and bulk nano-composite materials.* Experimental and theoretical studies of the thermoelectric properties of two-dimensional semiconductor and semimetal nanostructures and bulk nano-thermoelectric materials.

Those research were conducted jointly by NTU"KhPI" and Massachusetts Institute of Technology within the framework of CRDF and other projects



Ukrainian Coordinator of Projects:
Prof. E.I. Rogacheva, NTU"KhPI", Kharkov
US Coordinator of Projects:
Prof. M.S. Dresselhaus, Massachussets Institute of Technology, Cambridge, MA

The joint research projects with Massachusetts Institute of Technology (MIT)

1. US CRDF (2013-2015); Award Number: UKP2-7074-KK-12, Low-Dimensional and Bulk Nanocomposite Materials for Thermoelectric Energy Conversion;

2. US CRDF (2000-2002); Award Number: UE2-2069
   Physical Principles for Optimization of Thermoelectric Properties of IV-VI Based Superlattices;

3. US CRDF (2002-2004); Award Number: UP2-2426-KH-02 , Mechanisms Behind the Thermoelectric Properties of IV-VI-Based Low-Dimensional Structures and the Development of Materials with a High Figure of Merit;

4. US National Science Foundation (Division of Materials Research) and Ukrainian Fundamental Science Foundation; (*2008-2009*); UU24/014; Controlling thermoelectric properties of crystals and thin-film structures of bismuth-antimony solid solutions;

5. US National Science Foundation (Division of Materials Research) and Ukrainian Fundamental Science Foundation; (2011-2013); #UU 42/006 (Ф42/557-2011). Quantum Size Effects in Semiconducting V_2VI_3 and IV-VI- based Thin Film and Bulk Structures and Control of their Thermoelectric Properties;

6. US National Research Council's Twinning Program , (1999-2000), Award Number: NAS 93 INT-9522667
   Low-dimensional structures for thermoelectric applications.

The results of research carried out in the Laboratory were presented at International conferences in:

United Kingdom (1997),
Spain (1994),
Germany (1995, 2008, 2009),
USA (1997, 1999, 2003),
France (2002, 2003,2015),
Japan (1993,2003),
Australia (2004),
Taiwan (2005),
Austria (2006),
Brazil (2008),
Republic of Korea (2010),
Greece (2011),
Denmark (2012),
Switzerland(2009, 2012),
Estonia (2013),
The Netherlands (2013),
Ireland (2014),
China (2016),
Hong Kong (2016)

Main publications 2000--2005:

1. E.I. Rogacheva, Controlling Defect Structure and Properties of Complex Thermoelectric Materials, **Jpn J. Appl. Phys.** V.39.Suppl.39-1 (2000) pp.529-534.
2. E.I. Rogacheva, Tavrina T.V., Gladkikh L.I. Non-Stoichiometry and Defect Structure of $CuInSe_2$//**Jpn J. of Appl. Phys.** 2000. V.39.Suppl.39-1. P.397-398.
3. E.I. Rogacheva, Krivulkin I.M., Nashchekina O.N., Sipatov A.Yu., Volobuev V.V., Dresselhaus M.S. Effect of oxidation on the thermoelectricc properties of PbTe and PbS epitaxial films, **Appl.Phys.Lett.,** 2001, V.78. N.12.p. 1661-1663.
4. E.I. Rogacheva, Tavrina T.V., Grigorov S.N., Nashchekina O.N., Volobuev V.V., Fedorov A.G., Dresselhaus M.S. Effect of oxidation on the thermoelectric properties of PbSe thin films// **Journal of Electronic Materials,** .2002. Vol. 31. N 4. P. 298-303.
5. E.I. Rogacheva, Tavrina T.V., Nashchekina O.N.,.Grigorov S.N, Nasedkin K.A., Dresselhaus M.S., Cronin S. B. Quantum size effects in PbSe quantum wells// **Applied Physics Letters.** V.80, N 15, 2690-2693, 2002.
6. E.I. Rogacheva, O.N. Nashchekina, S.N. Grigorov, M. Us, M. Dresselhaus and S.B. Cronin, Oscillatory behavior of the transport properties in PbTe quantum wells, **Nanotechnology,** 2003, 14(1), p.53-59
7. E.I. Rogacheva, O.N. Nashchekina, T.V. Tavrina, M.Us, Mildred S. Dresselhaus, Steve B. Cronin, Oded Rabin, Quantum size effects in IV-VI quantum wells// **Physica E,** 2003, V.17, pp. 313-315
8. E.I. Rogacheva, S.N. Grigorov, A.G. Fedorov, T.V. Tavrina, N.A. Kalashnik,A.Yu. Sipatov, V.V. Volobuev, M.S. Dresselhaus. Study of growth mechanism and electrophysical properties of thin SnTe films and SnTe/EuS bilayers on KCl substrates, **Functional materials,** 2003, Vol. 10, N 4, pp. 676-681.
9. E.I. Rogacheva, S.N. Grigorov, O.N. Nashchekina, S.G. Lyubchenko, M.S. Dresselhaus, Quantum size effects in *n*-type Bi thin films, **Appl. Phys. Lett.** 2003, V.82, N. 16, pp. 2628-2630.
10. E.I. Rogacheva, Self-Organization Processes in Impurity Subsystem of Solid Solutions, J. **Phys. Chem. Sol.** 64 (2003) p. 1579-1583.
11. E.I. Rogacheva and T.V. Tavrina, Nonstoichiometry of CuInSe2 and Method of "Controlled Atomic Defects", **Journal of Physics and Chemistry Solids,** V. 64 (2003) pp. 1911-1915.
12. .E.I. Rogacheva, Non-Stoichiometry and Problem of Heavy Doping in Semiconductor Phases, **Materials Science in Semiconductor Processing,** V.6 (2003) pp. 491-496.
13. E.I. Rogacheva, S.G. Lyubchenko, M.S. Dresselhaus. Effect of oxidation on thickness dependences of thermoelectric properties in PbTe/mica thin films, **Thin Solid Films**.- 2005.- V. 476.- P. 391-395.
14. E.I. Rogacheva, S.G. Lyubchenko, S.N. Grigorov, Yu. Sipatov, V.V. Volobuev, M.S. Dresselhaus. Investigation of the growth mechanism, structure and thermoelectric properties of thin PbTe films grown on mica. **Function. Mater.** 2005. V.12. N1. P 21.
15. E.I. Rogacheva, A.A. Yakovleva, S.G. Lyubchenko, Plastic deformation instabilities in Bi crystals under microindentation, **"Functional materials",** Vol.12, No 3, pp.442-446, 2005.
16. E.I. Rogacheva, Non-stoichiometry and properties of ternary semiconductor phases of variable composition based on IV-VI compounds, **J. Phys. Chem. Solids,** 2005, V. 66, p. 2104
17. E.I. Rogacheva, S.G. Lyubchenko, Thermoelectric and mechanical properties of lead telluride doped with bismuth, J. **Thermoelectricity,** № 3, 2005, pp. 24-31.
18. E.I. Rogacheva, Grigorov S.N., Nashchekina O.N., Tavrina T.V., Lyubchenko S.G., Sipatov A.Yu., Volobuev V.V., Fedorov A.G., Dresselhaus M.S. Growth mechanism and thermoelectric properties of PbTe/SnTe/PbTe heterostructures // **Thin Solid Films**.- 2005. V. 493. P. 41-48.
19. E.I Rogacheva, Nashchekina O., Meriuts A., Lyubchenko S., Dresselhaus M., Dresselhaus G. Quantum Size Effects in n-PbTe/p-SnTe/n-PbTe Heterostructures, **Appl. Phys. Lett.** 2005. V. 86. P.063103

Main publications 2006 - 2011:

1. E.I. Rogacheva, S.G. Lyubchenko, O.S. Vodorez: Temperature dependences and isotherms of galvanomagnetic properties of Bi doped PbTe crystals and thin films. **Functional materials,** Vol. 13, № 4, pp. 571-576 (2006).
2. E.I. Rogacheva, O.N. Nashchekina: Non-stoichiometry and properties of SnTe<Cd> semiconducting phase of variable composition, ***Phys. Stat. Sol. (a)***, Vol. 203, № 11, pp. 2856-2860 (2006).
3. E.I. Rogacheva, A.A. Drozdova: Thermoelectric properties of polycrystalline bismuth-antimony solid solutions, *Journal of* ***Thermoelectricity***, № 2, pp. 22-28 (2006).
4. E.I. Rogacheva: Percolation effects and thermoelectric materials science. ***Journal of Thermoelectricity***, № 2, pp. 61-72 (2007).
5. E.I. Rogacheva, S.G. Lyubchenko, M.S. Dresselhaus: Semimetal-semiconductor transition in thin Bi films. ***Thin Solid Films***, Vol. 516, № 10, pp. 3411-3415 (2008).
6. E.I. Rogacheva, A.A. Yakovleva, V.I. Pinegin, M.S. Dresselhaus: Concentration anomalies of properties in Bi-Sb semimetalic solid solutions. ***J. Phys. Chem. Solids***, V. 69, N 2-3, pp.580-584 (2008).
7. E.I. Rogacheva: The problem of doping of non-stoichiometric phases. ***Journal of Physics and Chemistry of Solids***, Vol. 69, Nos 2-3, pp.259-268 (2008).
8. E.I. Rogacheva, A.A. Drozdova, I.I. Izhnin, M.S. Dresselhaus: Magnetic field dependences of galvanomagnetic properties of polycrystalline Bi-Sb solid solutions. ***Physica Status Solidi (A)***, Vol. 206, № 2, pp 298-302 (2009).
9. E.I. Rogacheva, S.G. Lyubchenko, O.N. Nashchekina, A.V. Meriuts, A.Yu. Sipatov, M. S. Dresselhaus: Quantum size effects and transport phenomena in Bi thin layers. ***Microelectronics Journal***, Vol. 40, № 4-5, pp. 728-730 (2009).
10. E.I. Rogacheva, S.G. Lyubchenko, A.A. Yakovleva, Effect of magnetic field on galvanomagnetic properties of mica/Bi/EuS heterostructures. ***Microelectron. Journal***, V. 40, № 4-5, p. 821-823 (2009).
11. E.I. Rogacheva, O.N. Nashchekina, A.Yu. Sipatov, A.G. Fedorov, S.N. Grigorov, T.V. Tavrina, and M.S. Dresselhaus: Growth mechanism and thermoelectric properties PbX/EuS (X - S, Se,Te) superlattices. ***Phys. Status Sol. C***, V. 6, № 5, p. 1149-1153 (2009).
12. E.I. Rogacheva: The Specificity of Structure and Electrical Behavior of Multinary Solid Solutions Formed by Chemical Compounds. ***Physica Status Solidi C***, Vol. 6, № 5, pp.1307-1311 (2009).
13. E.I. Rogacheva, A.A. Drozdova, O.N. Nashchekina, M.S. Dresselhaus, G. Dresselhaus: Transition into a gapless state and concentration anomalies in the properties of $Bi_{1-x}Sb_x$ solid solutions. ***Applied Physics Letters***, V. 94, № 20, p. 202111 (2009).
14. E.I. Rogacheva, A.A. Drozdova, and O.N. Nashchekina: Percolation effects in semimetallic Bi-Sb solid solutions. ***Physica status solidi (A)***, Vol. 207, № 2, pp 344–347 (2010)
15. E. Rogacheva, O. Vodorez, O. Nashchekina, A. Sipatov, A. Fedorov, S. Olkhovskaya, and M.S. Dresselhaus: Oscillatory behavior of the thermoelectric properties in *p*-PbTe quantum wells. ***J. Electronic Materials***, Vol. 39, № 9, pp. 2085-2091 (2010).
16. E.I. Rogacheva: Mechanism of “controlled atomic defects”: extension to the ternary systems. ***Japanese Journal of Applied Physics***, Vol. 50, № 5, p. 05FBO1 (2011).
17. E.I. Rogacheva, Dar’ya S. Orlova, Mildred S. Dresselhaus, and Shuang Tang: Size Effects in Bi-Sb Solid Solutions Thin Films. ***MRS Online Proceedings Library***, Vol. 1314, mrsf10-1314-ll10-02 (2011).
18. E.I. Rogacheva, Olga Vodorez, Vladimir Pinegin, and Olga Nashchekina: Evidence for Self-organization Processes in PbTe-Bi_2Te_3 Semiconductor Solid Solutions. ***Journal of Materials Research***, Vol. 26, № 13, pp. 1627-1633 (2011).
19. E.I. Rogacheva, O.S. Vodorez, O.N. Nashchekina, Influence of nonstoichiometry defects on the mechanism of impurities dissolution and thermoelectric properties of germanium monotelluride, ***J. of Thermoelectricity***, Vol. 4, pp. 22–31 (2011).

Main publications 2012 - 2016:

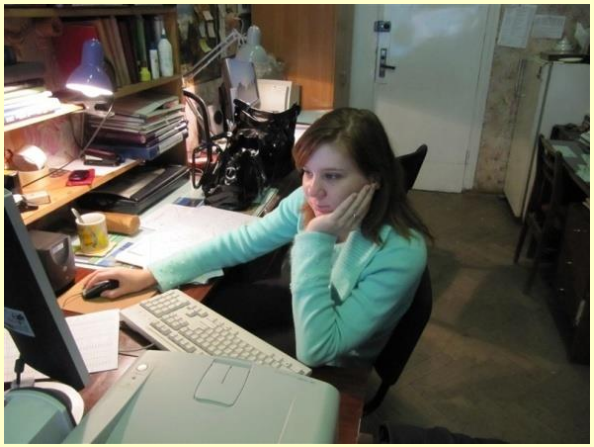
1. E.I. Rogacheva, D.S. Orlova, O.N. Nashchekina, M.S. Dresselhaus, S. Tang, Thickness dependence oscillations of transport properties in thin films of a topological insulator $Bi_{91}Sb_9$, **Applied Physics Letters**, 101, 023108 (2012).
2. E.I. Rogacheva, O.N. Nashchekina, S.I. Ol'khovskaya, and M.S. Dresselhaus, Size effects in PbSe thin films (J. Thermoelectricity, 2012, N 4).
3. E.I. Rogacheva: Nonstoichiometry and Properties of SnTe Semiconductor Phase of Variable Composition, in: Stoichiometry and Materials Science - When numbers matter, ISBN 978-953-51-0512-1, edited by Alessio Innocenti and Norlida Kamarulzaman 2012, pp. 105-144.
4. E.I. Rogacheva, O.S. Vodorez, and O.N. Nashchekina: Oscillations of transport properties in PbTe - Bi_2Te_3 solid solutions. **J. Phys. Chem. Solids**, 74, 35-39 (2013).
5. E.I. Rogacheva, O.S. Vodorez, Peculiarities of the concentration dependences of structural and thermoelectric properties in solid solutions PbTe-PbSe, **J. Thermoelectricity** 2013. Vol. 2. P. 61–73.
6. E.I. Rogacheva, Doroshenko A.N., Nashchekina O.N., Men′shov Yu.V. Thermal Conductivity in $Bi_{1-x}Sb_x$ Solid Solutions, **J. Electron. Mater.** 2013. V. 42, N7. P. 2098-2102.
7. E.I. Rogacheva, A.N. Doroshenko, V.I. Pinegin, M.S. Dresselhaus, Electronic phase transitions and structural instability in $Bi_{1-x}Sb_x$ solid solutions / **J. Thermoelectricity.** 2013. N 6. P. 13-20.
8. E.I. Rogacheva, Nikolaenko A.A. , Vodorez O.S. , Sipatov A.Yu., Grigorov S.N., Fedorov A.G.Size effects in GeTe thin films, **J. Thermoelectricity.** – 2014. Vol. 2. P. 11–21.
9. E.I. Rogacheva, Vodorez O.S. , Nashchekina O.N., Dresselhaus M.S. Peculiarities of the concentration dependences of thermal conductivity in $(PbTe)_{1-x}(Bi_2Te_3)_x$ semiconductor solid solutions, **J. Thermoelectricity.** 2014. V. 3. P. 49-59.
10. E.I. Rogacheva, Vodorez O.S. , Nashchekina O.N. , Dresselhaus M.S. Concentration anomalies of the thermal conductivity in PbTe-PbSe semiconductor solid solution, **Phys. Stat. Sol. B.** 2014. V. 251, N. 6. P. 1231-1238.
11. E.I. Rogacheva, A.V. Budnik, A.Yu. Sipatov, O.N. Nashchekina, and M.S. Dresselhaus, Thickness dependent quantum oscillations of transport properties in topological insulator Bi2Te3 thin films, **Appl. Phys. Lett.**, 106, 053103 (2015).
12. E.I. Rogacheva, O.N. Nashchekina, A.V. Budnik, M.V. Dobrotvorskaya, A.G. Fedorov, et.al. Growth and structure of thermally evaporated Bi2Te3 thin films, **Thin Solid Films**, 612 (2016) 128-134.
13. E.I. Rogacheva, A.N. Doroshenko, O.N. Nashchekina, and M.S. Dresselhaus, Specific heat critical behavior in $Bi_{1-x}Sb_x$ solid solutions, **Appl. Phys. Lett.** 109, 131906 (2016); doi: 10.1063/1.4963880

New physical effects have been revealed, in particular:

- ***In a number of solid solutions based on IV-VI, V_2VI_3 and other semiconductor compounds, and in Bi-Sb solid solutions we observed anomalies in the concentration dependences of properties at ~ 0.5-1 mol.% of the impurity. It was assumed that in any solid solution irrespective of the microscopic nature of the interimpurity interaction, there exist phase transitions of percolation type when a continuous chain of interactions between impurity atoms running through the entire crystal is formed. In this sense all solutions must behave in a universal way near a critical concentration x_c corresponding to the percolation threshold. The idea about the universality of the revealed effects is supported by a wide spectrum of the objects and properties studied.***

- ***For the first time, distinct oscillations in the thickness dependences of the thermoelectric properties of semiconductor IV-VI thin films were observed and attributed to size quantization of energy spectrum.***

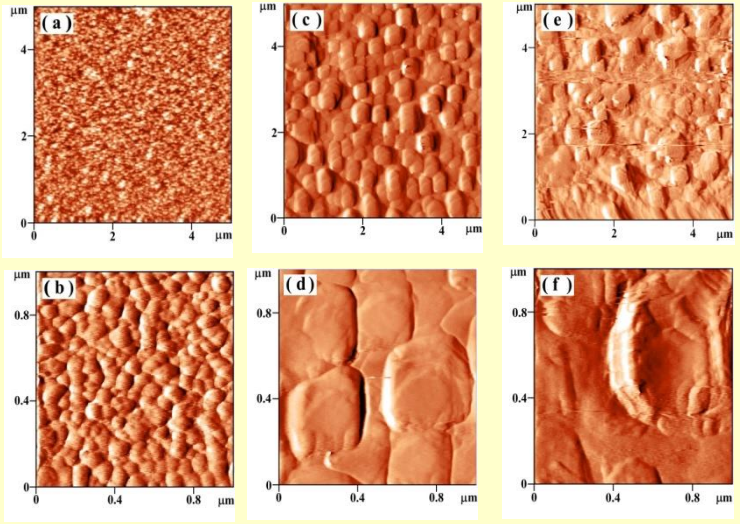
- ***It was established that the thickness dependences of the transport properties for topological insulator Bi_2Te_3 thin films exhibit an oscillatory behavior. The undamped character of these oscillations was attributed to the specificity of the surface states in topological insulators. The results demonstrates that surface states are indeed protected by time-reversal symmetry.***

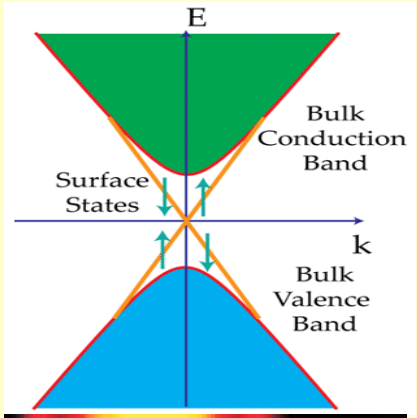


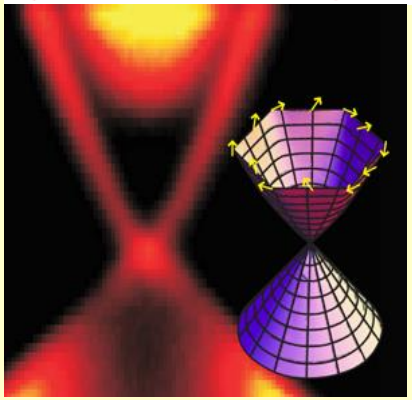
New Experimental Results

•Topological Insulators

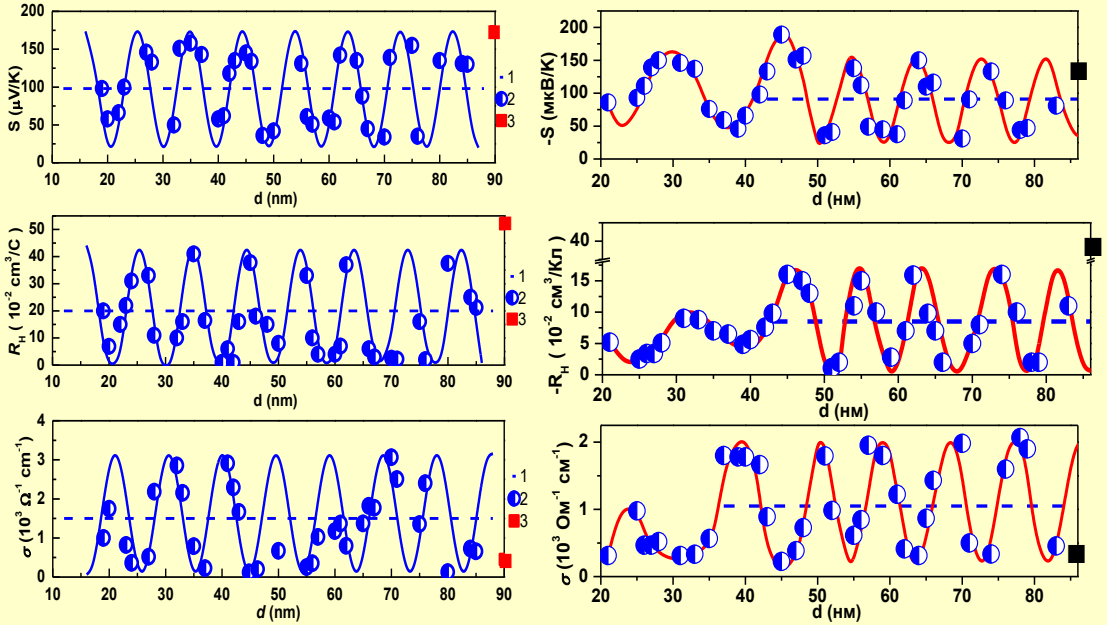
Morphology of p-Bi_2Te_3 thin films (AFM)







p-Bi_2Te_3



n-Bi_2Te_3

Proposals for cooperation:

1. Critical Phenomena of Percolation Type in Semiconductor and Semimetal Solid Solutions and Development of Thermoelectric Materials for Energy Conversion

The goal of research: **To prove the existence of critical phenomena accompanying the phase transition of percolation type from dilute solid solutions to an impurity continuum occuring in any solid solution and in the subsystem of the second phase particles; to study the mechanism and kinetics of such phase transitions, self-organization processes, the behavior of the thermoelectric properties within the critical ranges. The objects of the study are solid solutions based on IV-VI, V_2VI_3 and other compounds and the Bi-Sb solid solutions.**

Justification: **A wide use of solid solutions for practical applications, the existence of a great number of semiconductor devices based on heavily doped semiconductors (tunnel diodes, thermoelectric devices, etc.), a great potential of nano-heterostructures stimulate detailed studies of property-composition dependences.**

Expected impact: **The existence of the above mentioned critical phenomena of percolation type and self-organization processes should be taken into account when developing high efficiency thermoelectric and other materials by introduction of impurities, formation of solid solutions, nanostructured composites or low-dimensional structures .**

Proposals for cooperation:

2. Quantum Size Effects and Transport Phenomena in IV-VI and V_2VI_3 – based semiconductor nanostructures

The goal of research: **Theoretical and experimental study of the physical phenomena induced by the size quantization of electron and phonon spectra in IV-VI and V_2VI_3-based nanostructures (thin films, quantum wells, and super-lattices) by measuring transport properties. Study of the influence of various factors (band structure, carrier concentration, quantum well and barrier width, etc.) on the manifestation of quantum size effects. Development of theoretical models and main principles for controlling and optimizing the thermoelectric properties of IV-VI and V_2 VI_3 based nanostructures using quantum size effects.**

Justification: **Electron confinement in nanostructures leads to a radical change in physical properties as compared with bulk crystals. Theoretical predictions for a substantial increase in the thermoelectric figure of merit in low-dimensional structures under decreasing the quantum well or wire width stimulate interest in investigating quantum size effects in 2D-structures and detailed studies of properties as functions of width of the layers.**

Expected impact: **For thin film applications in thermoelectricity, it is necessary to take into account the quantum size effects, which can drastically change properties under thickness change. A decrease in the width of a quantum well can lead to a significant increase in thermoelectric figure of merit and, consequently to an increase in the efficiency of a thermoelectric converter.**

Proposals for cooperation:

3. Transport properties of topological insulators thin films

The goal of research: Theoretical and experimental study of the influence of topologically protected metallic surface states with a linear Dirac dispersion law in topological insulators (Tis) on electrophysical, thermoelectric and galvanomagnetic properties of the Bi_2Te_3, Bi_2Se_3 and $Bi_{1-x}Sb_x$ thin films and to study the influence of various factors (crystal structure, band structure, carrier concentration, film thickness, temperature, etc.) on these properties.

Justification: In topological insulators, a strong spin-orbit interaction leads to the appearance of topologically protected metallic surface states with a linear Dirac dispersion law. In contrast to ordinary metals in which surface states are easily violated by the defects, in TIs such states are topologically protected. The existence of such surface states has already been confirmed by using angle-resolved photoemission spectroscopy and scanning tunneling microscopy. However, up to date, there are significantly fewer experimental data on the peculiarities of the transport properties of the TIs. One can expect that the Dirac cone structure of the surface states will influence the transport properties of the films. Besides, Bi_2Te_3, Bi_2Se_3 and $Bi_{1-x}Sb_x$ are known to be the best low-temperature thermoelectric materials which are widely applied in the thermoelectric cooling devices.

Expected impact: The topological properties of Tis provides a broad potential for applications of TIs in microelectronics and computer technology. In recent years many works have appeared suggesting the possibility of using the properties of TIs in thermoelectricity. The obtained results will be important both for the development of the concepts of solid state physics and for practical applications of topological insulators.