MINISTRY OF EDUCATION AND RESEARCH OF THE REPUBLIC OF MOLDOVA

Ghitu Institute of Electronic Engineering and Nanotechnologies

Technology to prepare the single-crystals layers for thermoelectric applications (microcoolers)

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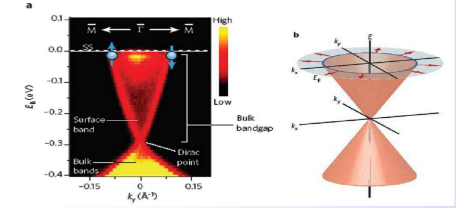
The primary purpose of the given presentation was to develop new reliable and reproducible engineering techniques to prepare low-dimensional structures (single-crystals layers) of bismuth telluride and semiconductor bismuth–antimony topological insulator (TI) *n*-and *p*-type for thermoelectric applications (microcoolers).

Single crystals of Bi_2Te_3 layers (1–20 µm) were prepared using the mechanical exfoliation method by cleaving a thin layer from bulk crystalline Bi_2Te_3 and $Bi_{1-x}Sb_x$ samples. Using a mechanical cleavage process, thin layers were separated from the crystalline bulk. The process was repeated several times to obtain layers with different thickness. To peel $Bi_{1-x}Sb_x$ layers off using an adhesive tape, the bulk sample was cooled to 70 K to increase the interatomic distance and thereby to provide a decrease in the interaction (Van der Waals) forces $P = m/d^2$ (patent). Using *p*- and *n*-type layers as *n*- and *p*-legs of a thermoelement, $\Delta T = 4°C$ was obtained at 300 K on a cross section of 1×10^{-4} cm². The use of a segmentation method (increasing the cross section as high as to a value of 5×10^{-4} cm²) made it possible to obtain $\Delta T = 8°C$ at 300K.

It is known that an increase in the temperature of the micro- sensor by 10°C leads to a twofold decrease the sensor durability.

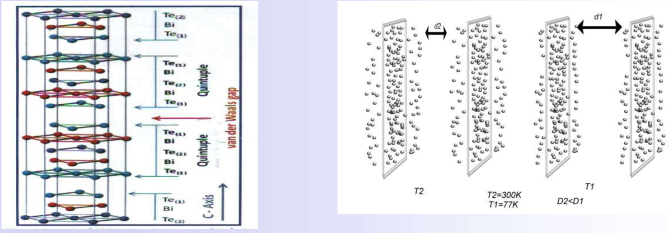
Our experimental samples the thermoelectric micro- coolers with efficient cooling capacity, small areas, short response time and with reproducible engineering techniques are in high demand on the telecommunication markets of the future.

Topological insulators, crystal structure Bi_2Te_3 and $Bi_{1-x}Sb_x$



(a) (b)

Fig1.(a)Electronic structure of Bi_2Se_3, obtained by ARPES. The electron energy E_B is deferred from the wave vector k_y. At the center of the Brillouin zone (point Γ), the surface zones give one Dirac point, which proves that this material is a topological insulator [3];
(b) is a theoretically idealized electronic structure of Bi_2Se_3, showing the spins of electrons with energy E as it moves along the Fermi surface with energy E_F [1].



(a) (b)

Fig.2, (a): Schematic of Bi_2Te_3 crystal structure of D_{3d}^5 -R(-3)m space group showing quintuple layers and location of the van der Waals gaps. The $Te^{(1)}$ -$Te^{(1)}$ bond is the weakest while the **Bi-Te$^{(1)}$** bond is the strongest. The mechanical exfoliation mostly results in breaking the $Te^{(1)}$ -$Te^{(1)}$ van der Waals bond and the formation of few quintuples layers. (b): Schematic representation of two adjacent **atomic bismuth antimony** layers at *T* = (*1*) 300 and (*2*) 77 K.

Technology of manufacturing single crystal Bi_2Te_3 and $Bi_{1-x}Sb_x$ layers.

To peel bismuth–antimony layers off using an adhesive tape, the bulk sample was cooled to 70 K to increase the interatomic distance (Fig. 2b) and thereby to provide a decrease in the interaction (van der Waals) forces $P = m/d^2$ (patent).

Patent MD 1366 Z 2020.03.31 Procedeu de obţinere a peliculelor monocristaline subcţiri
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Fig.3. Single crystal Bi_2Te_3 layer with four-contact and holder for the measurements thermo-power α=u/ΔT.

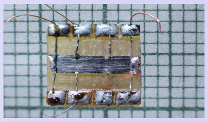
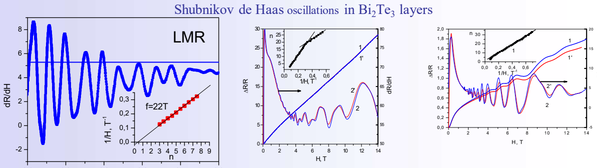


Fig. 4. Sample of $Bi_{1-x}Sb_x$ layer on the substrate of foil-clad paper-based laminate with soldered potential and Hall contacts.

Shubnikov de Haas oscillations in Bi_2Te_3 layers



$$f = [\Delta 1/H]^{-1} = \left(\frac{c}{2\pi e\hbar}\right) S(k_F)\,\frac{A(T_1,H_n)}{A(T_2,H_n)} = \frac{T_1}{T_2}\cdot\frac{sh\left(\frac{2\pi^2 m^* ckT_2}{|e|\hbar H_n}\right)}{sh\left(\frac{2\pi^2 m^* ckT_1}{|e|\hbar H_n}\right)},\ [1] \qquad \text{at } T_1 = \frac{T_2}{2}$$

$$m^* = \frac{|e|\hbar H_n}{4\pi^2 ckT_1}\,arch\left[\frac{A(T_1,H_n)}{A(2T_1,H_n)}\right], \qquad T_D = \frac{\hbar}{\pi k_B}\cdot\frac{1}{\tau}, \qquad \mu_S = \frac{\hbar e}{2\pi k_B}\cdot\frac{1}{m_e T_D},$$

$m_{C\parallel}$= 0.13m_0, $m_{C\perp}$= 0.11m_0, $T_D^1 = 1.3\,K, T_D^2 = 6\,K$, μ_S^1=2,3•10³ cm²/V•sec, μ_S^2=12,1•10³ cm²/V•sec

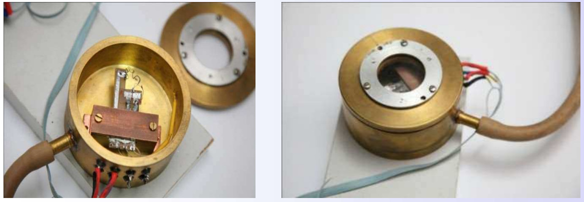
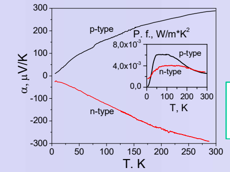


Fig. 7. Test device for measuring the temperature gradient ΔT of low dimensional thermoelectric materials.



ZT=α²σ/χ*T, P.f.=α²σ

T=300K

χ_{layer}=0.7*10⁻² W/cm*K [2, 3]
χ=0.8

Fig.6 Temperature dependencies of resistivity ρ(T) (a), thermopower α(T), and power factor P.f.=α²σ (inset) for Bi_2Te_3layer p and 2- n-type

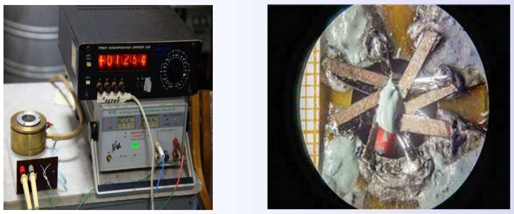


Fig. 8 Test setup for measuring the temperature gradient ΔT of thermoelectric materials.

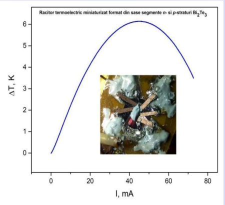


Fig. /9 Dependence of the temperature difference between the cooling layer (10 µm) and the substrate (T=300 K) on the input current

The advantages of the proposed recrystallization technology:

The developed technology for producing of single-crystal Bi_2Te_3 and Bi1-x Sbx TI layers with high thermoelectric efficiency has allowed a method of segmentation of the pairs consisting from n - and p-type layer to receive cooling 8⁰C, at 300K on the area1x10⁻⁴ cm , that can form base for creation of tiny cooling devices for (for high heat fiux cooling in electronic and optoelectronic systems;