Photon treatment effect on the surface and figure of merit of thermoelectric material Bi$_2$Te$_{3-x}$Se$_x$

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Abstract
The phase composition, structure, morphology, and thermal conductivity of Bi$_2$Te$_{3-x}$Se$_x$-based semiconductor solid solution after photon treatment (PT) were studied by X-ray diffractometry, SEM, TEM, and the laser flash techniques. It was revealed that PT leads to recrystallization of the subsurface layers of the solid solution with the formation of a heterogeneous nanocrystalline structure. The thermoelectric figure of merit of the semiconductor Bi$_2$Te$_{3-x}$Se$_x$ (n-type) solid solution increases after PT due to modification of the surface layers. This is due to the decrease of the thermal conductivity of the studied material after PT.

Keywords Photon treatment · Surface modification · Phase composition · Thermal conductivity · Figure of merit

Introduction
Semiconductor thermoelectric materials, based on Bi$_2$Te$_3$–Bi$_2$Se$_3$ and Sb$_2$Te$_3$–Bi$_2$Te$_3$ solid solutions, and having the high thermoelectric figure of merit ($ZT$), pose prospects in a wide range of applications in the devices, converting thermal energy into electrical energy at the temperature range of 300–600 K [1–5]. Specifically, great progress has been achieved in energy harvesting [6–8]. Nowadays, the efficiency requirements for thermoelectric materials have increased greatly. Thus, the task of maximizing the potential of these materials is of great interest. The main requirements, determining the high thermoelectric efficiency of the materials, have been already formulated by Ioffe [9]. According to these requirements, there are two ways to increase $ZT$: setting an appropriate elemental composition (the composition of the thermoelectric materials should maximize the ratio of electrical conductivity to the lattice thermal conductivity) and the creation of a structure, through the formation of a composite substructure, which includes nanocontacts between the macrocrystallites of a bulk phase [10]. The possible increase of $ZT$ through the variation of elemental composition is almost exhausted, while increasing $ZT$ by exploiting its structural dependence has a long-term perspective [11].

To date, several methods have been developed for obtaining bulk thermoelectric materials. Most of them such as the condensation in an inert gas atmosphere [12]; plasma chemical method [13]; chemical synthesis [14] followed by spark plasma sintering [15]; the grinding powders in a ball mill [16] are based on the compacting of powders with an appropriate composition. The main challenge in these approaches is to create the synthesis conditions of homogeneous bulk thermoelectric materials, not only maximizing the anisotropy of electrophysical properties of the bismuth telluride rhombohedral lattice but also increasing the mechanical properties (taking into account the low strength of these materials along the cleavage planes) [17]. The mechanical strength and adhesion of the switching layers are especially important for the production of thermoelectric generator modules, whose branches experienced high-temperature gradients [18]. As shown in [19], the mechanical polishing followed by the photon treatment (PT) through the irradiation of semiconductor surfaces by the powerful xenon lamps increases the
adhesion of a contact metallization to the semiconductor branches. PT initiates the recrystallization processes, which leads to the formation of a nanocrystalline structure in the subsurface layers of semiconductors [20]. It was shown that the formation of 15–20-nm-thick nanoplates (defects) in the Sb$_{2−x}$Bi$_x$Te$_3$ structure is accompanied by a 15% increase in $ZT$, compared to the “standard” material [21]. As demonstrated by calculations, in the nanostructured materials with the tunnel contacts between the particles or layers, the main mechanism of charge transfer is the quantum tunneling between nanoparticles. Besides, the phonon thermal conductivity through the barrier layers is absent [22]. Thus, the present work aimed to establish the PT treatment effect on the thermoelectric figure of merit of the Bi$_2$Te$_3$–Bi$_2$Se$_3$ solid solutions through the modification of the sample’s surface layer.

**Materials and methods**

The original semiconductor samples based on Bi$_2$Te$_3$–Bi$_2$Se$_3$ solid solution (n-type) were obtained by the cold pressing, followed by hot isostatic pressing of powders with the corresponding composition at $T=670$ K with the subsequent annealing at $T=570$ K for 24 h in an argon atmosphere. Figure 1 shows the cross-sectional SEM image of a semiconductor material synthesized by this method. In the isostatic pressing process, the volume structure of the material is ordered. The crystallites are preferably oriented and the $c$ axis coincides with the direction of the punch movement (see Fig. 1). The structure of the workpiece at a distance of 100–200 μm from the surface contacting with the wall of the matrix (mold) during pressing is different.

As follows from Fig. 1, the structure of a subsurface layer (up to 200 μm thick) contains the fractures and flat defects, resulting from the sliding of crystallites along the cleavage planes. The texture is formed by deformation in the polycrystalline sample (the crystallites are mainly oriented perpendicular to the pressing axis (see the selected fragment in Fig. 1). The texture formation occurs due to the plastic flow of the material (extrusion) along the mold surface. To investigate the heat conductivity, the as-prepared semiconductor billet was cut out into plates of 10 × 10 × 3 mm in size to ensure that their surface was parallel to the pressing axis (the selected fragment in Fig. 1 is the cut-out end).

The PT treatment of the sample’s surface was carried out by the UOL.P-1M experimental setup. The chamber is shown schematically in Fig. 2a.

The PT was alternately carried out by irradiation of both sides of a sample with the powerful radiation (spectral range $\lambda = 0.2–1.2$ μm, Fig. 2b) in an Ar atmosphere under the following modes: single and double irradiation with a packet of pulses with a duration of $10^{-2}$ s for 1.4 s (which corresponds to the radiation energy ($E_1$) ~ 140 J/cm$^2$ supplied to the sample).

**Fig. 1** The cross-sectional SEM image of the semiconductor material sample obtained in the process of hot pressing (the selected fragment is the end of the plate, cut out for the experiment)

**Fig. 2** The PT chamber (a) and the xenon lamp emission spectra of (b): 1, a sample; 2, xenon lamps; 3, quartz tubes; 4, sealing
The structural analysis was performed using a high-resolution transmission electron microscope (TEM, FEI Titan-300), a scanning electron microscope (SEM, FEI HELIOS Nanolab) and a powder diffractometer (XRD, Bruker D2 PHASER with a Cu Kα source) operated at 40 kV and 35 mA. The samples were prepared by the cross-section technique, using a focused ion beam (FIB, Ga+ with the energy of 30 keV). The energy-dispersive X-ray microanalysis (EDAM for SEM and transmission (STEM) electron microscopes) was used to map an elemental composition over the sample surface and the concentration profile of elements as a function of depth was obtained. STEM images were obtained by registering the low- and high-angle scattered electrons. The first method allows analyzing the grain substructure, and the second one reveals pores, grain boundaries, and their location throughout the layer thickness.

The thermal conductivity of the studied samples before and after PT was determined by a laser flash method with the use of a Netzsch LFA 467.

Results and discussion

Figure 3 shows XRD patterns of the Bi$_2$Te$_3$–Bi$_2$Se$_3$ samples (n-type) before and after PT.

It follows from the XRD data that the phase composition of the samples corresponds to a non-homogeneous solid solution Bi$_2$Te$_{3-x}$Se$_x$ (0.7 ≤ x ≤ 1.0), attributed to a rhombohedral lattice (R̃3m) with the lattice parameters $a$ and $c$ ranging from 0.4300 to 0.4339 nm and from 3.000 to 3.022 nm, respectively. The XRD spectra of the samples after PT differ from those for the as-prepared structures of the initial ones. The peaks’ intensity redistribution and a change in their width for the samples after PT can be caused by the surface layer recrystallization, leading to a decrease in stresses and the formation of grains with arbitrary mutual orientation. It is because the subsurface layer of the sample heats up to a temperature of about 800 K in the PT process.

Although the second PT does not change the diffraction maxima intensity, it leads to a decrease in the peak’s width, caused by an increase in the grain size during the recrystallization of the subsurface layer.

Figure 4 shows SEM images of the surface of a semiconductor material before and after doubly PT.

As follows from Fig. 4, the surface morphology of the semiconductor material is transformed greatly during the PT process. The initial surface (Fig. 4a) is characterized by the isotropic relief inhomogeneities, sized from 50 to 150 nm, resulting from the deformation compacting of the powder during the pressing process. The PT modifies the surface (Fig. 4b) with the formation of the anisotropic inhomogeneities with lateral dimension up to 1.5 μm, originated from the recrystallization of a submicron subsurface layer. The ultrafine particles (up to 30 nm in size) observed on the surface are sublimated from the material in the process of PT due to the condensation of volatile components.

Figure 5 shows the cross-sectional STEM, TEM images and the concentration profile of FIB elements for the semiconductor material after the doubly PT.

The structure of the sample surface layer with a thickness of ~500 nm after PT (Fig. 4a, b) differs from that in the bulk. A large-block polycrystalline structure with crystallites from 0.5 to 3 μm in size is observed at a distance of more than 1 μm from the surface. The substructure is characterized by...
flat and globular defects. The flat defects include a system of parallel lamellar inclusions with a width ranging from 50 nm to 1 μm and cracks of the same size. The globular inhomogeneities do not exceed 50 nm in size. The structure of the subsurface layer (modified in the phase transition process) is heterogeneous (Fig. 4a). Both the large arbitrary oriented crystallites ranging from 0.5 to 3 μm in size and nanocrystals with the size of ~15 nm are observed on the treated surface (see Fig. 4a). The modified layer demonstrates the high density (~2 × 10¹⁰/cm²) of globular defects (pores, inclusions), ranging in size from 15 to 40 nm. As seen in Fig. 4b, the crystallites (sized from 40 to 60 nm) in the top-most layer contain no dislocations and demonstrate a “core–shell” spherical morphology (see Fig. 5d). At a depth of more than 1.5 μm, the crystallites are significantly larger (d > 250 nm) and contain a network of dislocations with a linear density of about 1 × 10⁶/cm (see Fig. 5e).

It follows from the concentration profiles of elements in the samples after the PT treatment (Fig. 5c) that the subsurface region of 3 μm is enriched with Se and depleted by Te compared to the bulk material, where the elemental composition is close to that of the Bi₂Te₃₋ₓSeₓ solid solution for x ~ 1. The change in the elemental composition is caused by diffusion triggered by the high temperature at the sample surface and occurring during the PT process [19]. Some authors found that Te sublimation occurs in the PT process, leading to the formation of various defects (vacancies, nanopores) [20].

Figure 6 shows the thermal conductivity as a function of temperature for the studied samples. Experimental data shows that both the single and doubly PT treatments decrease the thermal conductivity. As regards the double PT, this decline is more prominent (4–5%) for the entire temperature range studied.

According to [23], the thermoelectric figure of merit can be calculated as $ZT = \frac{Tρ}{σκ}$ (where $T$, $σ$, $ρ$, and $κ$ are the absolute temperature, electrical conductivity, the Seebeck coefficient, and the thermal conductivity, respectively). Figure 7 shows how the calculated thermoelectric figure of merit of the studied samples varies with temperature taking into account the measured data for the Seebeck coefficient and electrical conductivity. As seen from Fig. 7, the magnitude of thermoelectric figure of merit does not change after the first PT despite the decrease in the heat conduction. It is because the conductivity $σ$ decreases by 2–5% depending
on temperature and the Seebeck coefficient $\alpha$ increases by 2.5% after the first PT. As was mentioned above, the size of the crystallites in the surface layer decreases under the first PT. Consequently, the observed changes in the material properties are caused by the change in the structure of a subsurface region.

The double PT of the studied samples leads to an increase in their ZT by 8%. In this case, the value of the thermal conductivity decreases by ~8%, and the $\sigma$ and $\alpha$ magnitudes change slightly. The Seebeck coefficient and conductivity increase by 1% and 2.5%, respectively, relative to the corresponding parameters of the studied samples after the first PT. Our attempts to increase the number of PT cycles lead to decreasing the figure of merit which resulted from the grain size increase induced by PPT.

Figure 8 shows the Seebeck coefficient as a function of temperature for the studied samples.

As seen from Fig. 8, the PT increases the Seebeck coefficient $\alpha$ (in magnitude). The single PT declines $\alpha$ by 2.5%. The second PT conducted with a higher pulse intensity further decreases $\alpha$ by 1%. The Seebeck coefficient is varied through the electronic density of states or by increasing the relaxation time through the scattering mechanisms. It was demonstrated theoretically that the band bending at the grain boundaries in polycrystalline materials scatter the low-energetic carriers, increasing $\alpha$ [24]. Apparently, this mechanism is responsible for the increase in the Seebeck coefficient magnitude in our case.

Figure 9 demonstrates the electrical conductivity as a function of temperature for the studied samples.

The electrical conductivity depends on the carrier concentration and mobility. Taking into account that the PT affects the mobility $\mu$ greater than the concentration, we can conclude that in our case the PT changes the $\mu$. In the polycrystalline materials, the scattering associated with inhomogeneities (grain boundaries, dislocations, point defects) contributes the mobility greatly. Thus, in our case the PT produces more scattering centers, reducing the carrier mobility and consequently the electrical conductivity. The second PT leads to the material re-crystallization, decreasing the scattering phenomena in the studied samples.

The quality factor increase after the second PT is also associated with the change of a crystal structure in the surface layers. As shown above, during the PT treatment of both sides of the semiconductor plates, a sandwich occurs. It contains the Bi$_2$Te$_{3-x}$Se$_x$ phase on the bulk and having a textured layered structure. In contrast, the near-surface regions (~570–600 nm) contain the Bi$_2$Te$_{3-x}$Se$_x$ phase with a heterogeneous structure composed of the nanocrystals ($d = 15$ nm).
and the arbitrarily oriented grains in the form of plates with the width ranging from 0.1 to 0.4 μm and the length from 0.6 to 4 μm. As a result, the crystalline structure is formed near the sample surface, with the gradient in average crystallite size, directed from the surface towards the material bulk. The average grain size varies from 50 to 300 nm at a distance of 1–2 μm from the surface. Thus, the fraction of grain boundaries in the bulk of the semiconductor differs by 30–40 times relative to that near the surface. It was reported [20, 25] that an increase in ZT in the nanostructured thermoelectric materials is originated from the decrease in the thermal conductivity caused by the phonon scattering on the nanosized inhomogeneities. In our case, the grain boundaries act as such inhomogeneities, occurring due to the segregation of impurity atoms and selenium that diffuses in the PT process. Due to the low electrical conductivity of selenium and the high fraction of grain boundaries, the Bi$_2$Te$_{1-x}$Se$_x$ crystallites can act as the macroscopic area within a semiconductor, having nano-size contacts in a matrix of low conducting material. Consequently, in the PT process, a gradient nanostructured region composed of the nanocrystals and large Bi$_2$Te$_{1-x}$Se$_x$ crystals with the tunneling contacts is created in the material.

The effective properties of Bi$_2$Te$_3$-based composites, with the nano-size contacts between macrocrystallites of the bulk phase, were theoretically studied in [7]. The proposed model of such nanostructured composite implies the occurrence of a tunnel contact at the boundary of the bulk and nanocrystalline phases. In the framework of this model and based on the field approximation, the effective values of the thermoelectric power, heat, and electrical conductivity, as well as the thermoelectric figure of merit, were calculated. It was found that when the tunnel contact width rises from 0.5 nm to 0.8 nm, the electron heat conductivity decreases by 3 times, the electrical conductivity declines, and the thermopower increases by about 10%. As a result, the authors reported the increase in ZT values up to 3.52. In our case, the PT modifies the only subsurface layers of the studied samples. Thus, the quantitative changes of the determined quantities were lower despite the qualitative coincidence with the measured results. Consequently, in our case, the increase in ZT can also be associated with the tunnel contact occurrence at the interface between the crystalline (the bulk of material) and nanocrystalline (subsurface layers of the material) phases.

**Conclusions**

The modified layer formed under the PT of semiconductor plates has an inhomogeneous nanocrystalline structure with an arbitrary nanocrystals’ orientation. By contrast, the bulk material demonstrates the stable elemental, phase composition and the large-block crystalline structure with an extrusion texture. The subsurface layers of semiconductor plates based on Bi$_2$Te$_3$–Bi$_2$Se$_3$ (n-type) solid solution occur in the process of PT, due to the recrystallization and modification. The gradient nanostructured area of the material is created, where the nanocrystals and large Bi$_2$Te$_{1-x}$Se$_x$ crystals represent a composite with the tunnel contacts. The formation of a gradient of the average grain size in the surface layers decreases the thermal conductivity and increases the thermoelectric figure of merit of the PT-treated material by 8%.

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**Compliance with ethical standards**

**Conflict of interest** The authors declare that they have no conflict of interest.

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