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INVESTIGATION OF Bi_2Te_3-$Bi_2Te_{3-x}S_x$ STRUCTURES BY PHOTOVOLTAGE MEASUREMENTS

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The single-cryslal structure of Bi_2Te_3-$Bi_2Te_{3-x}S_x$ with a p-n junction was prepared by the heat treatment of p-Bi_2Te_3 in sulphur vapors. This structure was characterized by the measurement of the photovoltaic effect. The dependence of the photovoltage at 77 K on the wavelength shows two peaks at 2.8 μm (= 0.44 eV) and at 1.9 μm (= 0.65 eV). The higher peak at 2.8 μm (= 0.44 eV) corresponds to the bandgap (E_g = 0.43 eV) of $Bi_8Te_7S_5$. It is created probably by the electric field on the p-n junction at the interface of n-$Bi_8Te_7S_5$ and deeper lying p-$Bi_2Te_{3-x}S_x$ with $x < 0.15$.

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Introduction

The Bi_2Te_3 crystals rank among the group of layered semiconductors of tetradymite structure (space group $D_{3d}^5 - R\bar{3}m$) and the compound is a component of materials applied in thermoelectric devices as solid state coolers or generators [1].

Substitution of Te atoms in $p\text{-}Bi_2Te_3$ by sulphur atoms can change the electrical conductivity from p- to n-type and thus in such a way it is possible to prepare a single-crystal structure of $Bi_2Te_3\text{-}Bi_2Te_{3-x}S_x$ with a p-n junction [2]. This structure was prepared by the heat treatment of $p\text{-}Bi_2Te_3$ in sulphur vapours which resulted in the formation of n-type $Bi_2Te_{3-x}S_x$ layer on the $p\text{-}Bi_2Te_3$ substrate. The change of the type of electrical conductivity was ascribed to the changes in the polarization of chemical bonds in Bi_2Te_3 lattice caused by the substitution of Te atoms by more electronegative sulphur atoms [2].

In this paper we have verified the technique of the preparation of p-n structure of $Bi_2Te_3\text{-}Bi_2Te_{3-x}S_x$ and investigated photovoltaic effect on these structure.

Experimental

Preparation and Basic Characterization of $Bi_2Te_3\text{-}Bi_2Te_{3-x}S_x$ Structure

The starting Bi_2Te_3 polycrystalline material was synthesized from the elements Bi and Te of 5N purity in evacuated conical silica ampoules at 1073 K for 48 hours. The growth of the single crystals was carried out in the same ampoules by means of a modified Bridgman method using a suitable temperature gradient 400 K/5 cm and a pulling rate of 1.3 mm h^{-1} [3].

The obtained single crystals, 50 to 60 mm in length and 8 mm in diameter, could be easily cleaved. Their trigonal axis c was always perpendicular to the pulling direction so that the (0001) plane was parallel to the ampoule axis. The orientation of the cleavage faces was carried out using the Laue back-diffraction technique which confirmed that these faces were always (0001).

Prism-shaped monocrystalline substrates about 1 mm thick were prepared by cleaving the Bi_2Te_3 crystals along the (0001) plane, and then exposing them at higher temperatures to sulphur vapour. After heat treatment in the sulphur atmosphere, the samples were cleaved in the centre of the prism along the (0001) plane. In this way samples with a gradient of sulphur-atom concentration were obtained. On one side of the prism there was an undoped $p\text{-}Bi_2Te_3$; on the opposite sulphur-treated side the tetradymite-type solution $Bi_2Te_{3-x}S_x$ was obtained (this can be deduced from the analysis of $Bi_2Te_3\text{-}Bi_2S_3$ phase diagram [4,5]). According to [2] this material shows n-type conductivity for $x > 0.15$. The

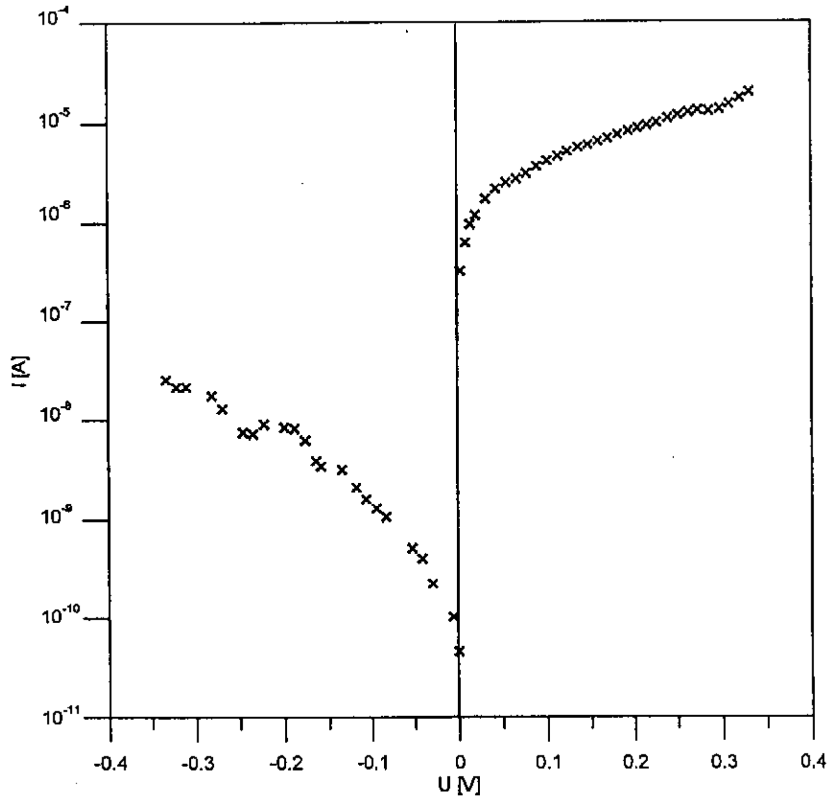

Fig. 1 Current-voltage characteristics of the p-n junction Bi_2Te_3-$Bi_2Te_{3-x}S_x$ at T = 294 K

presence of p-n junction in Bi_2Te_3-$Bi_2Te_{3-x}S_x$ structure is manifested by a typical course of current-voltage characteristics in Fig. 1. Analysis of the surface of the $Bi_2Te_{3-x}S_x$ layers carried out by electron microprobe gave the composition of 81.63 wt % Bi, 17.55 wt % S and 0.81 wt % Te. Composition of the surface layer can be expressed by the formula $Bi_2S_{2.8}Te_{0.03}$. The ratio of Bi to the atoms in the anion sublattice is given by the formula $Bi_2(S,Te)_{2.83}$. This means that the surface of the structure is formed by bismuth sulphide with a large deficit of sulphur, as compared to the stoichiometric formula of Bi_2S_3, and with a partial replacement of sulphur atoms by tellurium atoms. The analysis of X-ray „parallel beam" difractograms even indicates the presence of Bi_2S_3 structure.

Measurements of the Photovoltaic Effect

In order to obtain more information about Bi_2Te_3-$Bi_2Te_{3-x}S_x$ heterojunction, the photovoltaic effect (PV) measurements were carried out (see Fig. 2). Contactless

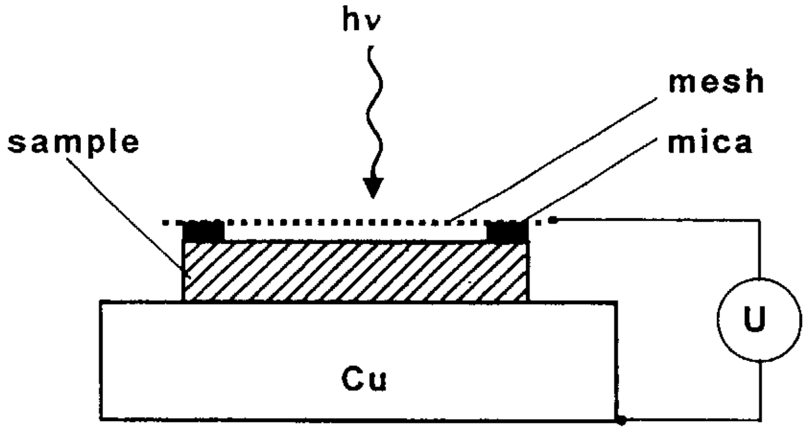

Fig. 2 Schematic arrangement of the photovoltage measurements

photoelectric method was used [6] to avoid any damage of the surface layer and also to exclude the dispersion in transmissivity of radiation caused by the contact. The sample was illuminated from the side of $Bi_2Te_{3-x}S_x$ through a metallic mesh. The mesh located in a small distance from the surface served as one electrode whereas a metal contact to Bi_2Te_3 was used as the opposite one. The spectral characteristics of the PV effect were measured using the photon flux which was maintained constant with help of the calibrated PbS detector. The monochromatic radiation was chopped and consequently alternating signal from the sample was generated.

Results and Discussion

The dependence of the photovoltage at 77 K on the wavelength of the prepared structure is shown in the Fig. 3, curve a. Two peaks were observed on the curve. One of them at 2.8 μm (= 0.44 eV) corresponds well to the bandgap (E_g = 0.43 eV) of $Bi_8Te_7S_5$. This semiconductor compound was for the first time identified in tetradymite type of solid solution by Soonpaa [7] who determined its bandgap from optical measurements.

As the concentration of sulphur in $Bi_8Te_7S_5$ expressed in mass units is 5.88% only, this compound must be located in the deepnes of the layer. Consequently, a high increase in sulphur concentration exists towards the surface. As the bandgap increases with an increasing sulphur concentration [2], there is a graded bandgap structure in the layer. It implies the presence of an internal electric field, which stimulates the photovoltaic effect. Besides this field there is another electric field on the p-n junction created at the interface of n-$Bi_8Te_7S_5$ and deeper

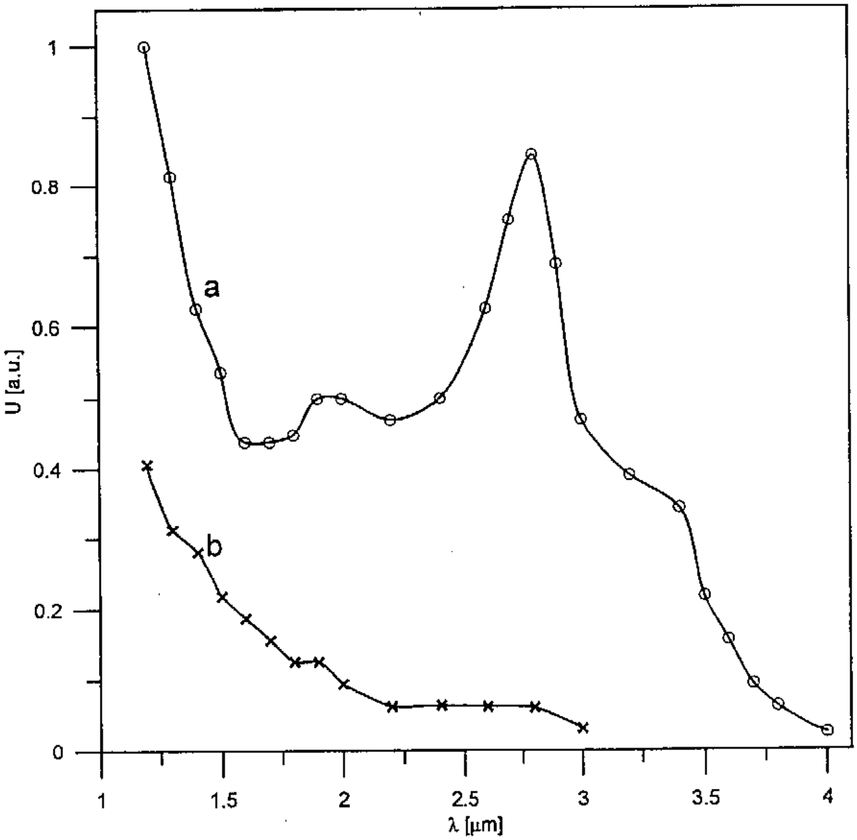

Fig. 3 a – spectral response of photovoltage from Bi_2Te_3-$Bi_2Te_{3-x}S_x$ structure measured at $T = 77$ K; b – the same after etching in 5% bromine in methanol solution

lying p-$Bi_2Te_{3-x}S_x$ where $x < 0.15$. It gives rise to the peak at $\lambda = 2.8$ μm. Another isotype junction is formed between $Bi_8Te_7S_5$ (tetradymite structure — rhombohedral space group D^5_{3d}-$R\bar{3}m$) and solid solution on the basis of Bi_2S_3 (orthorhombic space group D^{16}_{2h}-Pbnm), which was found on the surface of layer as $Bi_2S_{2.8}Te_{0.03}$. We assume that photons absorbed at this boundary cause the smaller peak at $\lambda = 1.9$ μm (= 0.65 eV).

The etching in of the samples in the solution of 5% bromine in methanol for 5 seconds removed several tenths of μm of the surface layer. The photovoltaic signal after that process decreased substantially, and its spectral response was represented by a smooth curve without any peaks (Fig. 3, curve b). The $Bi_8Te_7S_5$ compound is no more present within the layer and sulphur which probably penetrated into Bi_2Te_3 caused a small change in the bandgap of the tetradymite solution only.

Conclusion

The observation of the photovoltaic effect on the Bi_2Te_3–$Bi_2Te_{3-x}S_x$ structure in the infrared spectral region makes it possible to propose a new application of Bi_2Te_3 beside its traditional field of thermoelectric devices, i.e. the application of Bi_2Te_3–$Bi_2Te_{3-x}S_x$ structures in the construction of photovoltaic detectors of IR radiation.

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