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Thickness oscillations of the transport properties in *n*-type Bi_2Te_3 topological insulator thin films

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ABSTRACT

The dependences of the electrical conductivity, Seebeck coefficient and Hall coefficient on the thickness ($d = 20$–155 nm) of the *n*-type thin films grown on the glass substrates by the thermal evaporation in vacuum of the *n*-type Bi_2Te_3 topological insulator crystals have been measured. It has been established that these dependences have an oscillatory character with a substantial amplitude. The obtained results are interpreted in terms of quantum size effects, taking into account the peculiar properties of the surface layers of the Bi_2Te_3 films connected with the topological insulator nature of the bismuth telluride.

1. Introduction

Topological insulators (TIs) are a recently discovered class of objects of quantum physics which represent insulators with metallic surface states protected by time reversal symmetry [1,2]. Despite the relatively recent prediction [3–5] and subsequent experimental discovery [6–14] of TIs, at present there are already a lot of works on theoretical and experimental investigation of these objects of solid-state physics. This is connected with unique properties of these materials, which are of interest both from the point of view of the development of general physics concepts and because of their potential for practical use. Among such properties is the non-sensitivity of the TIs to the effect of nonmagnetic impurities or disorder. The unique properties of surface states are associated with a strong spin–orbit interaction coupling, which leads to a rigid connection between direction of the driving force on the surface electron and the orientation of its spin; the electron spin is perpendicular to its momentum. The constraint on the spin orientation of the surface electrons prevents backscattering for the metallic surface states. The topological properties of this material can persist up to high temperatures, which 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 [15–23]. However, up to now, the number of studies revealing the specificity of the transport properties in TIs connected with their TI nature has been relatively small, which is mainly associated with the problem of separating the conductivity within the metallic layer from the bulk conductivity. From this point of view, TI thin-film nanostructures are of particular interest because their large surface-to-volume ratio enhances the contribution of surface states to the total conductivity.

In nanostructures, the manifestation of quantum size effects (QSEs) is possible, because the dimensions of the system become comparable with the de-Broglie wavelength. Electron confinement in low-dimensional structures leads to a radical change in the physical properties of these systems as compared with bulk crystals and, in principle, the electron confinement introduces additional ways for controlling the properties of solids. In quantum wells, charge carrier motion is confined in one direction, which results in the quantization of the electron quasi-momentum and energy spectrum in this direction, and consequently, determines a quantum-mechanical scenario for various physical phenomena.

One of the manifestations of the QSEs in thin films is an oscillatory behavior of the thickness dependences of the kinetic and thermodynamic characteristics of the degenerate electron gas caused by the size quantization of the electron energy spectrum and drastic changes in the density of states on the Fermi surface when the Fermi level passes through different subbands [24]. Such quantum oscillations of the galvanomagnetic properties were observed and interpreted theoretically for semimetallic thin Bi films [25–27]. Later we observed an oscillatory behavior of the thermoelectric (TE) and galvanomagnetic properties in a number of IV–VI semiconductor compounds [28–33], which belonged to the best medium-temperature TE materials [34,35]. One can expect analogous effects in other semiconducting compounds.

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Taking into account the significant role that boundary conditions play in the description of processes in quantum systems, it can be suggested, that the particular quantum state of the electrons in the surface layers of TIs that result in the high stability of these states, will influence manifestation of QSEs because these special states cannot be damaged by the presence of defects of different types. That is why studying thickness oscillations in the transport properties of TI thin films is of interest. In the present work the objects of study are thin *n*-type Bi_2Te_3 films.

The Bi_2Te_3 semiconductor compound and Bi_2Te_3-based solid solutions are presently the best low-temperature TE materials, and these materials are extensively used in manufacturing refrigerant devices of different types [34,35]. Bi_2Te_3 crystallizes in a rhombohedral structure of tetradymite type, characterized by a nine-layer packing of Te atoms (space group R3m-D^5_{3d}) [34,35]. The rhombohedral lattice of the tetradymite type can be considered as a hexagonal laminated layered structure, in which a unit cell represents the consecutive stacking of three quintuple layer groups, in which the alternation of layers occurs according to the scheme: Te–Bi–Te–Bi–Te. The bonding between different quintuple layers is of a weak van der Waals type, although the Bi–Te bonding is stronger than the bonding between the layers [34,35]. The Bi_2Te_3 compositional homogeneity region in the Bi–Te system is small and corresponds to 59.75–60.2 at.% Te at 770 K [36]. It was established that in the Bi_2Te_3 homogeneity region, the *p*-type conductivity takes place; with increasing Te concentration up to ~62 at.% Te in the two-phase region (Bi_2Te_3 + Te) the inversion of the conductivity sign ($p \rightarrow n$) occurs, and near this composition, the highest values of the TE figure of merit are observed [34,35].

Recently, it was established that Bi_2Te_3 is classified among the 3D topological insulators [1,2,9,10,37]. These TI materials are characterized by their topologically protected spin-polarized surface states which lie in the fundamental band gap and gapless surface states which are protected by time-reversal symmetry. Until now there have been practically no works on studying the quantum thickness oscillations in this compound. We are aware of only one work [38], in which the authors observed oscillations in the dependences of the Hall mobility and concentration charge carriers on the thickness d (d = 10–300 nm) of the films prepared by the pulsed laser deposition from a Bi_2Te_3 target on Si substrates. However, the thin films compositions in this work did not correspond to stoichiometric Bi_2Te_3: Bi/Te ratio in the films varied from 1.15 to 1.23 while the ratio in ideal Bi_2Te_3 is 0.66. As the oscillation period (Δd = 40 nm) determined experimentally by the authors was close to bismuth Δd, they suggested that the thickness oscillations were connected with Bi excess in the films, mainly the existence of the BiTe compound. In the recently published work [39] we reported that in the films exhibiting a *p*-type conductivity, obtained by thermal evaporation of the stoichiometric *p*-Bi_2Te_3 crystals in vacuum, in the thickness range d = 18–600 nm, distinct sustained thickness oscillations of the TE properties are observed. We attributed the existence of the oscillations to the size quantization of the hole gas and suggested that the sustained character of these oscillations is connected with specific properties of the surface topological layer. It was of interest to find out whether the type of conductivity can influence the effects observed in [39].

The goal of the present work is to study the room temperature dependences of the TE and galvanomagnetic properties on the thickness of *n*-Bi_2Te_3 thin films grown on glass substrates, with the aim of revealing the quantum oscillations, and establishing the possible influence of the peculiar properties of the topological surface states on the manifestation of the quantum oscillations.

As a result of the studies carried out in the present work, we found out that the dependences of the transport properties on the *n*-Bi_2Te_3 film thickness in the range d = 20–150 nm, similarly to the *p*-Bi_2Te_3 films in [39], exhibit an oscillatory behavior. We also attributed these oscillations to the manifestation of QSEs in the *n*-Bi_2Te_3 thin films. We believe that the large oscillation amplitude, the sustained character of the oscillations and the substantial range of the thicknesses over which these oscillations are observed, are connected with the specific boundary conditions associated with TI nature of the *n*-Bi_2Te_3 compound.

2. Experimental details

The *n*-Bi_2Te_3 thin films with thicknesses in the range of d = 20–155 nm were prepared by thermal evaporation in an oil-free vacuum (10^{-5}–10^{-6} Pa) and the subsequent deposition on a freshly cleaved glass substrates at the temperature $T_S = 490 \pm 5$ K followed by annealing at 490 K during 1 h. The condensation rate was 0.1–0.3 nm/s. The choice of the technology for preparing Bi_2Te_3 films was based on our previously reported results [40,41]. In [40], it was established that using Bi_2Te_3 crystals with different stoichiometry as initial materials, one can control the conductivity type of the films, by applying a simple method of thermal evaporation from a single source. That is why for obtaining films with *n*-type conductivity, we used a sample with Te excess (62.8 at.% Te) as the initial crystal. The layer thicknesses, condensation rate, and surface roughness were controlled using a calibrated quartz resonator. The calibration of the resonator was performed with the help of an interferometer, and in the range of small thicknesses, for the thickness determination we used diffraction patterns of small angle X-ray scattering for Bi_2Te_3 films by comparing experimental and calculated X-ray diffraction patterns. The error of determining d did not exceed ±5%. The film roughness varied within 2–5 nm. The chemical compositions of the samples were determined by Energy Dispersive X-ray Spectroscopy (INCA Energy 350) in a Scanning Electron Microscope (SEM — JEOL JSM-6390 LV) using Si(Li) X-ray detector with energy resolution of 133 eV at accelerating voltage of 20 keV, operating in point with accuracy of 0.5 at.%, and by X-ray Photo-Electron Spectroscopy (XPS-800 Kratos). The XPS studies showed that the thickness of the oxidized surface layer did not exceed 1.5–2.0 nm and practically did not change in the process of aging at room temperature.

The crystal structures were characterized by X-ray powder diffraction (XRD) study using a DRON-2 diffractometer and Ni-filtered Cu Kα-radiation. The in-plane electrical conductivity σ and the Hall coefficient R_H were measured using a direct current and a magnetic field of 0.8 T on bulk parallelepiped-shaped samples and double Hall-cross shaped thin films. Six ohmic contacts were prepared by soldering indium to the film surface. The error in the R_H and σ measurements did not exceed ±5%. The Seebeck coefficient S was measured relative to Cu with an accuracy of ±3%. The measurements were carried out at room temperature on freshly prepared films extracted from the vacuum chamber to air. Three to four films with the same thicknesses were prepared within the same technological cycle and the difference in the obtained values of the kinetic coefficients usually did not exceed the errors of the measurement of these characteristics, indicating a good reproducibility of the experimental results. All films exhibited *n*-type conductivity.

3. Results

In Fig. 1, X-ray diffraction patterns for the initial bulk bismuth telluride material with 62.8 at.% Te and some of the obtained thin films are presented. The X-ray diffraction pattern for the bulk crystal contains lines corresponding to Bi_2Te_3 and the plane indices are in agreement with ASTM values for Bi_2Te_3 (Card No. 15-863) [42]. Besides, in the X-ray diffraction pattern for the crystal, an additional very weak line at $\theta = 23.06^0$ corresponding to the most intensive Te line (1 0 0) is seen; the rest of the Te lines with smaller intensities overlap with Bi_2Te_3 lines. In the XRD patterns for thin films, there are only Bi_2Te_3 lines, while Te lines are not observed. This is connected, perhaps, with some loss of Te in the process of evaporation and condensation of the initial material, although the preservation of the electronic type of conductivity in the films shows that the Te loss, if it occurs at all, is insignificant. It is also seen from the XRD patterns that the relative intensities of