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Dependence of electrical conductivity on Bi_2Se_3 thin film thickness

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Effect of film thickness d on electrical conductivity σ of n-Bi_2Se_3 thin films (d = 25–420 nm) prepared by thermal evaporation in vacuum onto glass substrates was investigated. It was established that the electrical conductivity increases with increasing of the thin films thickness. The observed effect is explained as a manifestation of the classical size effect connected with diffuse scattering of electrons at the thin film interfaces. The experimental $\sigma(d)$ dependence is satisfactorily described using the Fuchs-Sondheimer theory for the film thickness $d > 60$ nm. The specularity parameter and value of electrons mean free path are determined based of the experimental data.
Keywords: bismuth selenide, thin film, thickness, electrical conductivity, classical size effect.

Исследовано влияние толщины d на величину электропроводности σ тонких пленок n-Bi_2Se_3 (d = 25–420 нм), полученных методом термического испарения в вакууме с последующим осаждением на стеклянные подложки. Установлено, что электропроводность увеличивается по мере роста толщины тонких пленок. Наблюдаемый эффект поясняется как проявление классического размерного эффекта, связанного с диффузным рассеянием электронов на интерфейсах тонкой пленки. Экспериментальная зависимость $\sigma(d)$ удовлетворительно описывается в рамках теории Фукса-Зондгеймера на участке толщин $d > 60$ нм. На основе экспериментальных данных определены параметр зеркальности и значение средней длины свободного пробега электронов.

Залежність електропровідності від товщини тонких плівок Bi_2Se_3. *С.І.Меньшикова, О.І.Рогачова, О.Ю.Сіпатов, О.Г.Федоров.*

Досліджено вплив товщини d на величину електропровідності і тонких плівок n-Bi_2Se_3 (d = 25–420 нм), які отримано методом термічного випаровування у вакуумі з наступною конденсацією на скляні підкладки. Встановлено, що електропровідність збільшується зі зростанням товщини тонких плівок. Виявлений ефект пояснюється як прояв класичного розмірного ефекту, пов'язаного з дифузним розсіянням електронів на інтерфейсах тонкої плівки. Експериментальна залежність $\sigma(d)$ задовільно описується у рамках теорії Фукса-Зондгеймера на ділянці товщин $d > 60$ нм. На основі експериментальних даних визначені параметр дзеркальності та значення середньої довжини вільного пробігу електронів.

1. Introduction

Bismuth selenide (Bi_2Se_3) belongs to a group of narrow-band semiconductor of V_2VI_3 compounds, which are widely used in thermoelectricity [1–3]. Theoretical prediction [4, 5] and subsequent experimental evidence of an enhancement in the thermoelectric (TE) figure of merit in the low-dimensional structures based on V_2VI_3 [6] compared with the bulk crystals attracts attention to study of their properties in thin films. Increased interest to the V_2VI_3 materials study is also associated with manifestation of topological insulators properties in them [7, 8].

The properties of the material in the low-dimensional state can drastically differ from the crystal properties. Classical (CSE) and quantum (QSE) size effects can be observed in thin films. The first connected with diffuse scattering of charge carriers at the film interfaces and can be revealed in the case when the film thickness d is comparable with the mean free path of the charge carriers. QSE is due to quantization of energy spectrum of the charge carriers and is observed in the case when the value of d becomes comparable to the de Broglie wavelength λ_F [9]. Thickness oscillations in the transport properties of Bi_2Te_3 thin films of p- and n-type conductivity were observed in [10, 11] at room temperature, and were connected with the quantization of the energy spectrum of hole and electron gases. Manifestation of the size effects is important to take into account at predicting the material properties in the low-dimensional state.

Bi_2Se_3 thin films were obtained by various methods: molecular beam epitaxy [12, 13], chemical deposition [14, 15], thermal evaporation [16–20], etc. Usually the Bi_2Se_3 films grow on glass substrates [19]. The Bi_2Se_3 films prepared by thermal evaporation in vacuum usually have thicknesses $d > 50$ nm [16, 18, 20]. In [16], by this method the Bi_2Se_3 thin films in the thickness range $d = 50$–546 nm on the glass substrates were grown. The authors observed a sharp increase in the region $d = 50$–120 nm and a weak growth of σ at $d > 120$ nm. The authors attributed the rapid decrease of σ with decreasing the film thickness in the region $d < 120$ nm by the presence of high concentration of structural defects (discontinuities, voids) at initial stages of the film growth. An increase in σ with the film thickness in the region $d > 120$ nm the authors attributed to manifestation of the classical size effect and described dependence $\sigma(d)$ in the framework of the Fuchs-Sondheimer theory (FST). However, the grown films had very low values of the TE parameters: the Seebeck coefficient $S = 6$–11 μV/K and the electrical conductivity $\sigma = 10$–510 $\Omega\cdot$cm^{-1}, which indicated the lack of reproducibility of the crystal composition in the film state.

The goals of the present work is to obtain thin films of bismuth selenide in a wide thickness range by method of thermal evaporation of Bi_2Se_3 crystals in vacuum and to study effect of film thickness on the electrical conductivity value.

2. Experimental

Bi_2Se_3 thin films were grown by thermal evaporation of Bi_2Se_3 polycrystals in vacuum (10^{-5}–10^{-6}) from a tungsten boat at 620 K and the subsequent deposition onto glass substrates at (500±5) K. Before deposition, the substrates surface was subsequently purified with acid, distilled water and alcohol. The condensation rate was 0.1–0.15 nm/s. For simultaneous preparation of several films with different thickness, three holders at different distances from the evaporator were used. The film thicknesses were in the range of $d = 25$–420 nm. The film thickness and the condensation rate were controlled by a calibrated quartz resonator. The resonator was calibrated using the small angle X-ray diffraction techniques (for the films with thicknesses $d < 100$ nm) and by using the MII-4 interferometer (for the films with thickness $d > 100$ nm). Accuracy of measuring the film thickness d by using the MII-4 interferometer was ±10 %. The method of small angle X-ray diffraction made it possible to determine the film thickness to within ±0.5 nm. For the fixed film thickness d the results of the measurements by interferometric and X-ray diffraction methods were compared, and calibration curves of d in dependence on change in oscillation frequency Δf of the quartz resonator during the deposition of the material on the substrate were constructed.

The samples phase composition was determined by X-ray diffraction using the X-ray diffractometer DRON-2.0 with the Bragg-Brentano focusing geometry in filtered radiation of a copper anode.

Measurements of the Seebeck coefficient S were carried out with a temperature gradient of 10 K in the film plane relative to Cu with accuracy of ±3 %, and the electrical conductivity σ was measured using a conventional dc method with an error not exceeding ±5 %. The measurements were carried out on the freshly prepared samples at room temperature. The crystal samples were made in the form of a parallelepiped with dimensions of 10×2×3 mm, and the films — in the form of a double Hall cross.

3. Results and discussion

Results of X-ray diffraction of the crystal and thin films with different thicknesses indicated the presence of peaks corresponding to bismuth selenide phase, peaks of other phases were not detected.

In accordance with the results of the Seebeck coefficient measurements, the stoichiometric Bi_2Se_3 polycrystal exhibits *n*-type conductivity, which agrees with the literature data [21] and associated with shift of the maximum on the liquidus and solidus curves from stoichiometry to Bi excess side in the Bi–Se system. The Seebeck coefficient and electrical conductivity of the crystal were $S = -(63\pm2)$ μV/K and $\sigma = (1250\pm60)\ \Omega\cdot cm^{-1}$. Bi_2Se_3 thin films exhibit also *n*-type conductivity and were conduct in the investigated thickness range. The value of $S \approx -(55\pm2)$ μV/K in the films was lower than in the crystal.

In Figure 1, the electrical conductivity dependence on thickness is presented. It is seen that the values of σ for films obtained in the present work by the same method as in [16] are almost 3 times higher over the entire studied thicknesses range.

As can be seen from Fig. 1, the thickness dependence of σ (d = 25–420 nm) has a non-monotonic character: with increasing thickness to $d \sim 60$ nm, the value of σ sharply increases, and at $d > 60$ nm — the rate of σ rise decreases and the electrical conductivity of the films approaches the bulk value of σ.

The observed dependence of σ on thickness for the Bi_2Se_3 thin films can be explained by the manifestation of CSE. Taking into account that the electron gas in the films is degenerate, an attempt to describe the σ(d) dependence in the framework of the FST for metals was made [22]. In this theory, the specularity parameter p, characterizing the proportion of electrons elastically scattered by the film interfaces, is introduced. The value of p lies between 0 (for the entirely diffuse scattering) and 1 (for the entirely specular reflection). In the case when the electrons reflection from the film interfaces is completely specular, the CSE will not be observed. As a model, the FST considers a metal with the spherical Fermi

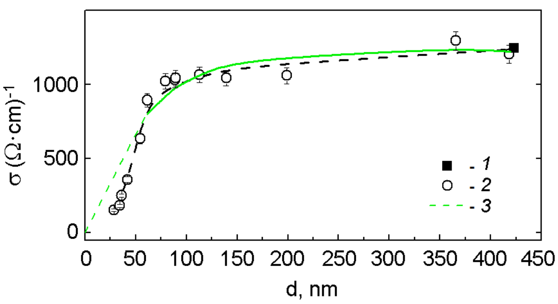

Fig. 1. Thickness dependences of electrical conductivity σ for thin films Bi_2Se_3: *1* — crystal; *2* — thin films; *3* — theoretical calculation accordance with equation (2).

surface and isotropic mean free path l of the charge carriers. A number of simplifying assumptions number of additional simplifications are used in the FST: the thin film structure does not depend on the thickness; the values of p and l are independent of d; p is constant and similar for both interfaces, independent of the incidence angle on the surface, and the electron trajectories; the dispersion law is quadratic [23].

The value of metal plate electrical conductivity in dependence on the film thickness in the FST framework is given as [22]:

$$\sigma_d = \frac{\sigma_\infty}{1 + \frac{3}{8}(1-p)\frac{l}{d}}, \quad d \ge l, \qquad (1)$$

$$\sigma_d = \sigma_\infty \cdot \frac{3}{4} \cdot \frac{1+p}{1-p} \cdot \frac{d}{l} \cdot \ln\frac{l}{d}, \quad d < l, \qquad (2)$$

where σ_∞ is conductivity of an infinitely thick film (bulk crystal).

Using the MatLAB 6.5 mathematical package, programs describing the experimental dependence σ(d) by equations (1) and (2) were written. In the programs, the values of p and l are varied. The calculation carried out for the thickness range d = 25–420 nm gave unsatisfactory results: in the field $d < 60$ nm the experimental character of the dependence σ(d) was different from the theoretical one. Therefore, the calculation for the thickness range d = 60–420 nm (Fig. 1) using equations (1) and (2) was made. The results showed that the experimental dependence σ(d) is best described using equations (2) and with $p = 0.59\pm0.02$ and $l = (710\pm40)$ nm (Fig. 1, line 3).

A sharp rise in σ with d increasing in the thickness range $d < 60$ nm can be explained by simplifications used in the FST (the constancy of l, the same value of the specularity parameter for the both surfaces, etc.).

4. Conclusions

It is shown that method of thermal evaporation of stoichiometric n-Bi_2Se_3 crystals in vacuum with subsequent condensation on glass substrates allows to obtain thin films (starting from thickness d = 25 nm) with the same composition and type of conductivity.

It is stated that electrical conductivity of the films increases with increasing film thickness, which is associated with manifestation of the classical size effect. The theoretical interpretation of the experimental results in the framework of the Fuchs-Sondheimer theory is given. A satisfactory agreement between the experimental data and the results of the theoretical calculation on the basis of the Fuchs-Sondheimer model for the thickness range d = 60–420 nm is observed. The deviation of the experimental dependence $\sigma(d)$ at the field $d < 60$ nm from the theoretical prediction is associated with a number of simplifications made in the calculation. Based on the experimental data, the specularity parameter ($p = 0.59$) and the mean free path of electrons ($l = 710$ nm) in the n-Bi_2Se_3 films were determined.

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