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Resistivity of thin bismuth films under in-plane tensile strain

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Abstract. The unique properties of bismuth and bismuth-antimony have attracted extensive attention in scope of strain engineering and straintronics in 2D materials in the past few decades. In this work we tested the technique of measurement of electric properties of bismuth films on glass and silicon substrates deformed by dome bending method. The obtained results show fine agreement with the investigation of films deformed by others techniques and can be used to model in-plane tensile deformation. Considering the use of two substrates of silicon and borosilicate glass, the method makes it possible to obtain continuously changed deformation of film in range up to 0.8 % of relative change of area at room temperature.

Keywords: bismuth, thin films, tensile deformation, resistivity, glass substrate, silicon substrate

Introduction

In recent years, interest in studying the effects caused by the influence of deformation on the physical properties of materials has revived again due to the development of straintronics (Bukharaev et al. 2018). In this regard, semimetals and narrow-gap semiconductors based on bismuth are of particular interest, since transport properties of bismuth films are significantly affected by various factors, in particular, deformations (Aguilera et al. 2015; Suslov et al. 2019b; Wu et al. 2018). This is due to the peculiarities of the bismuth band structure, which is characterized by a small indirect overlap of the valence and conduction bands (~40 mEv), as well as a small direct band gap (~15 mEv) (Jezequel et al. 1997). These features make it possible to smoothly change the parameters of the band structure of the samples during deformation and, consequently, to control their properties. From the experimental point of view, it is of interest to study the effect of in-plane strains on the transport properties of films since, firstly, significant strains can be obtained in the film state, which are not achievable in the bulk crystal (Suslov et al. 2022). Secondly, such deformations are quite easy to create in films since it was shown that the film on the substrate is in a deformed state at temperatures different from the producing temperature due to mismatch between the thermal expansion coefficients (CTE) of the film and the substrate (Suslov et al. 2019a).

In (Hirahara et al. 2012), based on ab-initio calculations, bismuth films on substrates with different lattice constants in the trigonal plane were simulated. The first principle calculations (based on the density functional theory (DFT)) of band structure of a bulk bismuth under various deformations in the trigonal plane were carried out. The strong influence of deformation on the band structure of the material was shown. Under compressive strain in the trigonal plane the energy overlap increased, while under tensile strain it decreased until a semiconductor gap appeared. With DFT, it was shown in (Wu et al. 2018) that, under uniaxial compressive strain of a bulk bismuth along the C_3 axis, a semimetal–semiconductor transition occurs in the region of the lattice constant ratio c/a = 2.41–2.51 with a maximum band gap at c/a = 2.45. In this state, an increase in the Seebeck coefficient and a decrease in thermal conductivity are expected, which, despite a decrease in conductivity, lead to an increase in ZT, which is one of the most important tasks in the development of thermoelectric converters.

As shown in numerous studies, bismuth films on various substrates grow predominantly in such a way that the trigonal axis of the crystal is perpendicular to the substrate plane (Jankowski et al. 2017; Krushelnitckii et al. 2017; Rodil et al. 2017). Thus, the deformations observed in the film samples are compressive or tensile strains in the trigonal plane. Due to the mismatch between the CTE of bismuth and various substrates, both compressive and tensile strains can be obtained. By combining this method and the method of substrate dome bending, it is possible to significantly expand the range of the created deformation (Suslov et al. 2022).

The paper presents the results of a study of the strain dependences of the bismuth films resistivity on borosilicate glass and silicon substrates, which undergo auxiliary in-plane tensile deformation by dome bending of substrate.

Experimental methods

The films were produced in high vacuum (up to 10^{-5} Torr) on borosilicate glass and silicon substrate by thermal evaporation. The surface of silicon substrate was oxidized (the thickness of oxide layer was approximately 1 um). It is shown that the size of bismuth film crystallites can significantly affect the transport properties of charge carriers (Komarov et al. 2019). Thus, oxidizing is crucial because it makes it possible to obtain the similar crystal structure of bismuth films on glass and silicon substrates.

In order to improve crystalline quality of the films, it was produced at 393 K with subsequent annealing at 523 K in 1 hour. During the annealing, the processes of recrystallization and coalescence occur, which lead to enlargement of crystallite size, reducing of crystallographic axes misorientation in adjacent crystallites and mechanical stress relaxation. Therefore, the annealing temperature is considered as the temperature of film formation.

The surface morphology was investigated by means of NT-MDT Solver Pro P47 atomic force microscope (AFM) of Herzen University shared core facilities in semicontact mode. In order to highlight the crystalline boundaries, the chemical etching with nitric and acetic acids solution was used (Demidov et al. 2017).

The crystal structure was investigated by X-ray diffraction (XRD) analysis technics by means of X-ray diffractometer DRON–7 of Herzen University shared core facilities using the classical Bregg-Brentano (θ–2θ) geometry. The shift of diffraction lines, corresponding to the trigonal plane of the single-crystal, indicates the change in the *c*-lattice constant (in the hexagonal elementary cell).

As mentioned previously, the discrepancy of the CTE of the film and the substrate leads to in-plane deformation at the temperature different from the formation temperature. The relative in-plane film area deformation can be expressed as

$$\frac{\Delta S}{S} = e^{2\int_{T_f}^{T} \alpha_s dT - \alpha_f dT} - 1$$

where α_s, α_f—substrate and film materials' CTEs, T_f—film formation temperature.

Table 1 shows the relative deformation of thin bismuth films on borosilicate glass and silicon substrate at 300 K and 77 K according to the above-mentioned formula as well as CTE of the used materials. The CTE of bismuth is anisotropic, so Table 1 shows its value in the trigonal plane. The CTE of borosilicate glasses has a wide range of values, so it was measured directly on the substrates used.

Table 1. Thermal expansion coefficients of materials

	α, 10^{-6} K^{-1}	ΔS/S at 300 K, %	ΔS/S at 77 K, %
Silicon	2.64*	0.47	0.95
Borosilicate glass	7.8	0.18	0.38
Bismuth	11.2**	—	—

Note: *—(Batchelder, Simmons 1964; Roberts, White 1986); **—(Cave, Holroyd 1960; Bunton, Weintroub 1969).

The range of tensile deformation can be expanded by auxiliary mechanical deformation of substrate, e. g., dome bending of the substrate. The method of dome bending is described in (Suslov et al. 2022) and based on stretching of the outer surface of the bended substrate on which the film is deposited. In the first approximation, the film deformation can be considered as an in-plane tensile strain, since the bending curvature radii are quite large and the film area is relatively small. The scheme of substrate bending is shown in Fig. 1.

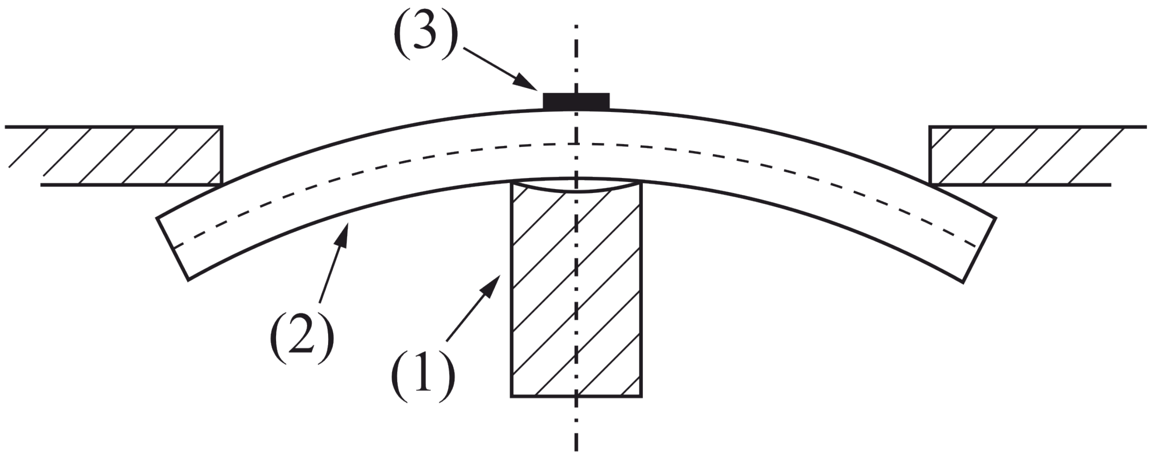

Fig. 1. The scheme of dome bending of the substrate. (1) shaft; (2) substrate; (3) deposited thin film

In the work we significantly improved the mechanical rigidity of the device for dome bending of the substrate. That made it possible to clearly determine the starting moment of dome bending.

In the framework of this work we investigate the resistivity of thin films relative to temperature and magnitude of deformation. The measurements were performed on samples powered by constant current at constant temperature. Temperature dependencies were obtained in the range of 77–300 K. Magnitude of in-plane deformation by dome bending corresponds to 0.8 % by area.

Results and discussion

By means of XRD analysis the preferential orientation of the trigonal axis of texture was determined to be perpendicular to the surface plane. Lattice constants *c* indicate that the silicon substrate stretches the film stronger than the glass substrate.

Fig. 2 shows the surface morphology of films on glass and silicon substrates. Despite the similarity of the average crystallite size, there is enhanced misorientation of the trigonal axis in films on the silicon substrate. It is shown clearly by the shape of grow figures—the deviation from the equilateral triangle shows the inclination of the trigonal axis. But the deviation does not exceed 15°, which was found out by means of XRD. The average size of film crystallites on both substrates is 2–3 μm in the entire range of investigated thicknesses, i.e., it exceeds the film thickness. The same size of crystallites ensures

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the same ratio of the contributions of the scattering of charge carriers on the film surface and grain boundaries in films on different substrates (Komarov et al. 2019).

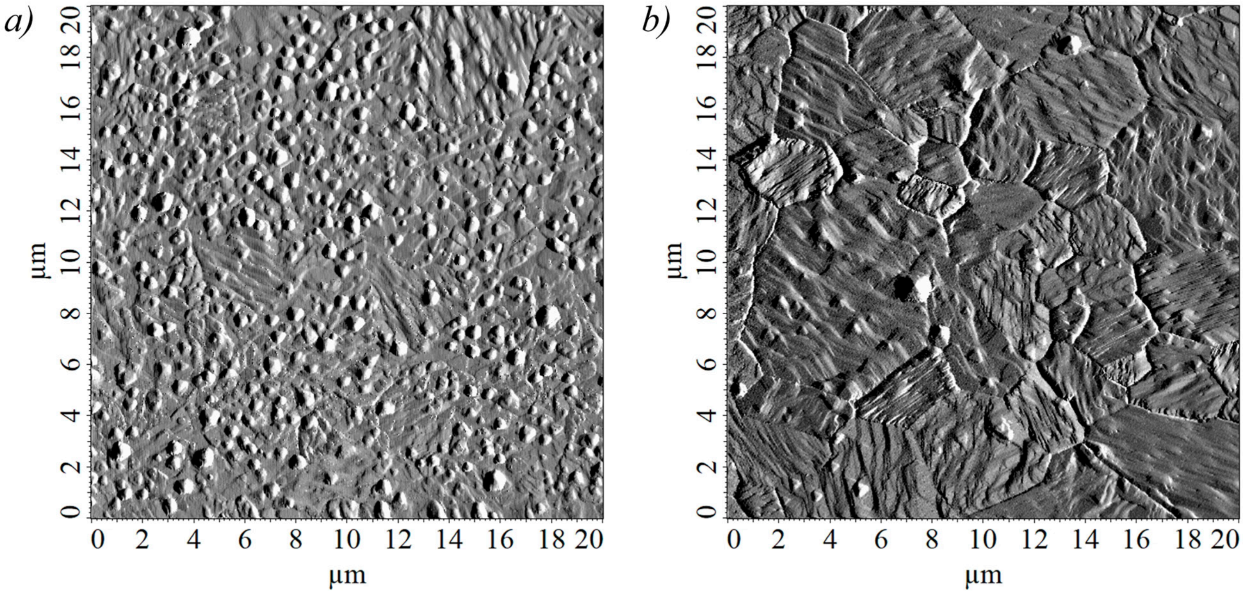

Fig. 2. AFM scan of 1000 nm thick bismuth film on (a) glass substrate; (b) silicon substrate

Fig. 3 shows the temperature dependencies of resistivity, relative to the value at 300 K, of bismuth films on glass and silicon substrates. Such representation allows to eliminate from analysis the difference of resistivity due to the difference in the crystal structure. The films on the silicon substrate have enhanced resistivity relative to resistivity on the glass substrate. The difference increases as the temperature decreases. It strongly correlates with the increase of deformation magnitude due to the difference in CTE of substrates.

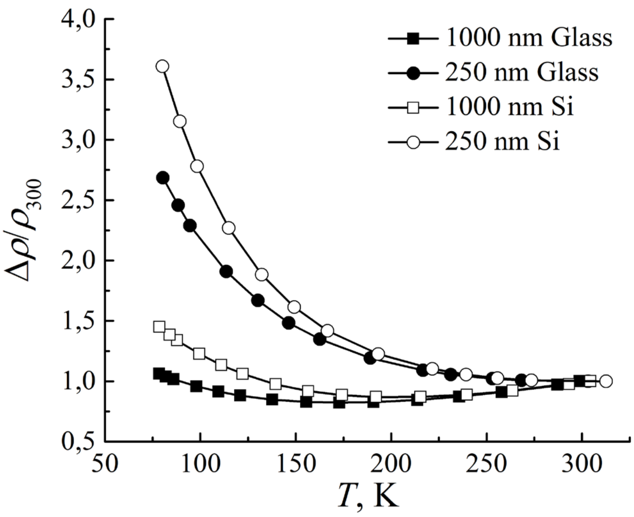

Fig. 3. Temperature dependencies of resistivity of bismuth films of 1000 nm and 250 nm thickness on the glass and the silicon substrate

The dependence of resistivity on deformation produced by dome bending is shown in Fig. 4 by example of 1000 nm bismuth films. The magnitude of deformation expressed as relative change of film area and was calculated by formula (1) and indirectly confirmed by XRD, according to *c*/*a* ratio (Suslov et al. 2022). The resistivity increases with increasing magnitude of deformation. Considering the thickness of the films, the resistance increases by approximately 0.12 Ohm by percent of relative area stretch. Because of difference in the crystal structure, there is a shift of resistivity in the film on silicon. However, the slope of curves shows possibility of their "stitching". So, by using two substrates of silicon and glass, one can obtain the continuous film deformation in the range of magnitude up to 0.8 % (by area) at room temperature. At the temperature of 77 K the deformation produced by difference of the film and substrate CTEs increases, consequently, the range of deformation magnitude is supposed to be exceeded.

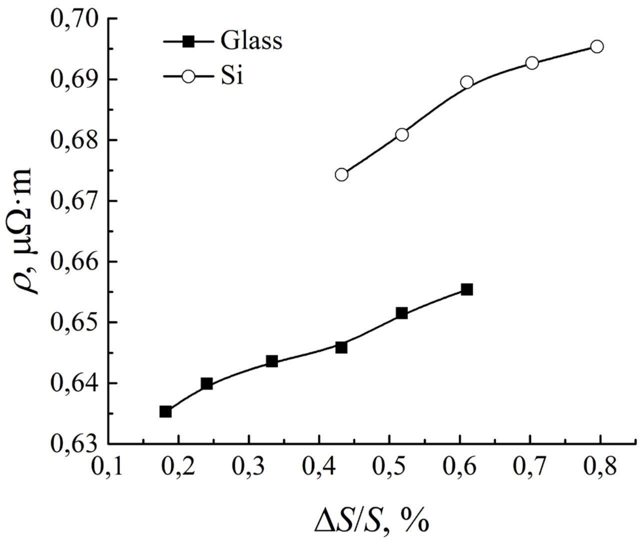

Fig. 4. The dependence of resistivity of bismuth film of 1000 nm thickness on glass and silicon substrates in condition of dome bending

The authors propose one more way to ensure the relevancy of using the dome bending method to model the in-plane tensile deformation by investigation of the crystal structure of films on bended substrates at temperature 77 K by means of XRD, but it is beyond the scope of this work.

Conclusions

In this work we tested the technique of measurement of electric properties of films on glass and silicon substrates deformed by dome bending method. The obtained results show fine agreement with resistivity data of thin films on different substrates and indicate the relevancy of using the dome bending method to expand the range of thin films tensile deformation relative to deformation occurred due to difference in CTE of film and substrate materials.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

Anton Suslov—development of a setup for measurements of the films transport properties under conditions of the substrate dome bending, XRD, data analysis, editing; Vasilisa Gerega—data analysis, preparation of the manuscript and figures; Matvey Glebov—samples producing, AFM and electrical properties measurements; Vladimir Grabov—editing, supervision; Vladimir Komarov—research concept development, data analysis, editing, supervision. All authors have read and agreed to the published version of the manuscript.

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References

Aguilera, I., Friedrich, C., Blügel, S. (2015) Electronic phase transitions of bismuth under strain from relativistic self-consistent GW calculations. *Physical Review B*, 91 (12), article 125129. https://doi.org/10.1103/PhysRevB.91.125129 (In English)

Batchelder, D. N., Simmons, R. O. (1964) Lattice constants and thermal expansivities of silicon and of calcium fluoride between 6 and 322 K. *The Journal of Chemical Physics*, 41 (8), 2324–2329. https://doi.org/10.1063/1.1726266 (In English)

Bukharaev, A. A., Zvezdin, A. K., Pyatakov, A. P., Fetisov, Y. K. (2018) Straintronics: A new trend in micro- and nanoelectronics and materials science. *Physics-Uspekhi*, 61 (12), 1175–1212. https://doi.org/10.3367/ufne.2018.01.038279 (In English)

Bunton, G. V., Weintroub, S. (1969) The thermal expansion of antimony and bismuth at low temperatures. *Journal of Physics C: Solid State Physics*, 2 (1), article 116. https://doi.org/10.1088/0022-3719/2/1/317 (In English).

Cave, E. F., Holroyd, L.V. (1960) Thermal expansion coefficients of bismuth. *Journal of Applied Physics*, 31 (8), article 1357. https://doi.org/10.1063/1.1735842 (In English)

Demidov, E. V., Komarov, V. A., Krushelnitckii, A. N., Suslov, A. V. (2017) Measurement of the thickness of block-structured bismuth films by atomic-force microscopy combined with selective chemical etching. *Semiconductors*, 51 (7), 840–842. https://doi.org/10.1134/S1063782617070065 (In English)

Hirahara, T., Fukui, N., Shirasawa, T. et al. (2012) Atomic and electronic structure of ultrathin Bi(111) films grown on Bi_2Te_3(111) substrates: Evidence for a strain-induced topological phase transition. *Physical Review Letters*, 109 (22), article 227401. https://doi.org/10.1103/PhysRevLett.109.227401 (In English)

Jankowski, M., Kaminski, D., Vergeer, K. et al. (2017) Controlling the growth of Bi(110) and Bi(111) films on an insulating substrate. *Nanotechnology*, 28 (15), article 155602. https://doi.org/10.1088/1361-6528/aa61dd (In English)

Jezequel, G., Thomas, J., Pollini, I. (1997) Experimental band structure of semimetal bismuth. *Physical Review B*, 56 (11), 6620–6626. https://doi.org/10.1103/PhysRevB.56.6620 (In English)

Komarov, V. A., Grabov, V. M., Suslov, A. V. et al. (2019) The Hall and seebeck effects in bismuth thin films on mica substrates in the temperature range of 77–300 K. *Semiconductors*, 53 (5), 593–598. https://doi.org/10.1134/S1063782619050105 (In English)

Krushelnitckii, A. N., Demidov, E. V., Ivanova, E. K. et al. (2017) Dependence of the surface morphology of ultrathin bismuth films on mica substrates on the film thickness. *Semiconductors*, 51 (7), 876–878. https://doi.org/10.1134/S1063782617070211 (In English)

Roberts, R. B., White, G. K. (1986) Thermal expansion of fluorites at high temperatures. *Journal of Physics C: Solid State Physics*, 19 (36), 7167–7172. https://doi.org/10.1088/0022-3719/19/36/008 (In English)

Rodil, S. E., Garcia-Zarco, O., Camps, E. et al. (2017) Preferential orientation in bismuth thin films as a function of growth conditions. *Thin Solid Films*, 636, 384–391. https://doi.org/10.1016/j.tsf.2017.06.048 (In English)

Suslov, A. V., Gerega, V. A., Grabov, V. M. et al. (2022) Deformation of thin films of semimetals by the dome bending method of the substrate. *Semiconductors*, 56 (1), 22–24. https://doi.org/10.1134/S1063782622020142 (In English)

Suslov, A. V., Grabov, V. M., Komarov, V. A. et al. (2019a) Methods of experimental studying the galvanomagnetic properties of thin semimetals films under conditions of plane stretch. *Journal of Physics Conference Series*, 1281 (1), article 012084. https://doi.org/10.1088/1742-6596/1281/1/012084 (In English)

Suslov, M. V., Grabov, V. M., Komarov, V. A. et al. (2019b) The thermoelectric power of $Bi_{1-x}Sb_x$ films ($0 \le x \le 0.15$) on mica and polyimide substrates in the temperature range of 77–300 K. *Semiconductors*, 53 (5), 589–592. https://doi.org/10.1134/S1063782619050257 (In English)

Wu, C. Y., Han, J. C., Sun, L. et al. (2018) Effects of trigonal deformation on electronic structure and thermoelectric properties of bismuth. *Journal of Physics. Condensed Matter*, 30 (28), article 285504. https://doi.org/10.1088/1361-648X/aacab9 (In English)