MOVPE growth and transport characterization of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ filmsP.I. Kuznetsov^{a,*}, G.G. Yakushcheva^a, B.S. Shchamkhalova^a, V.A. Jitov^a, A.G. Temiryazev^a, V.E. Sizov^a, V.O. Yapaskurt^{a,b}^a Kotelnikov Institute of Radio Engineering and Electronics, Russian Academy of Sciences, Fryazino, Moscow District 141190, Russia^b Department of Petrology, Geological Faculty, Moscow State University, Leninskie Gory, 119991 Moscow, Russia

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ABSTRACT

We present a first study of films of the quaternary $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ solid solutions on (0001) sapphire substrates grown by atmospheric pressure MOVPE. Trimethylbismuth, trimethylantimony, diisopropylselenide and diethyltelluride were used as precursors. To passivate the free bonds of the substrate and to improve the epitaxy, a thin (15 nm) ZnTe buffer layer was first grown. EDX analysis of the films grown at a temperature of 445 °C and about 10-fold excess of chalcogen in the vapor phase indicates on their compliance with V_2VI_3 stoichiometry. AFM and SEM investigations showed that at the initial stage of deposition the Stranski-Krastanov growth mode is dominant. Complete coalescence of nanoislands occurs at a thickness about 60 nm and further film formation is in the 2D layer-by-layer growth mode. A high mole fraction of antimony in the vapor phase leads to bad crystalline quality of the films and even to their discontinuity. Transport properties of the $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ films were evaluated using Van der Pauw Hall effect measurements in the range of temperatures of 10–300 K. Some films are always n- or p-type; in other samples the change of conductivity from p- to n-type was observed when the temperature decreases.

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1. Introduction

Topological insulators (TI) with non-trivial conducting topological surface electron states (TSS) are of current interest to researchers in physics of condensed matter and materials science. Binary compounds Bi_2Te_3 , Bi_2Se_3 and Sb_2Te_3 are considered as classical examples of three-dimensional (3D) TIs [1,2]. But bismuth and antimony chalcogenides are naturally doped semiconductors with high enough bulk conductivity due to unintentional doping by the native defect-induced charge carriers. In the case of Bi_2Se_3 Se vacancies supply electrons, in Bi_2Te_3 and Sb_2Te_3 excess metal occupies the Te lattice sites and acts as p-type dopant. Even advanced fabrication such as molecular beam epitaxy do not eliminate doping centers. To realize the novel transport properties of TIs associated with their topological surface states, it is necessary to reduce the contribution of bulk states to conductivity. One way to achieve this goal is mixing of Bi_2Te_3 , Bi_2Se_3 and Sb_2Te_3 and growing ternary $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ compounds. This allows one to significantly reduce the bulk conductivity [3–5] due to compensation of two types of carriers. In MBE grown $\text{Bi}_{1.06}\text{Sb}_{0.94}\text{Te}_3$ well-developed

quantum Hall effect (QHE) arising from TSS has been observed recently [6].

Today the quaternary $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ solid solutions (BSTS) with tetradymite structure are considered as the best platform to get TIs with true insulating bulk. In 1961 Teramoto and Takayanagi [7] showed that certain compositions of quaternary solid solutions have a high resistivity and a low carrier concentration. In 2011 Ren et al. [8] carried out a systematic study of transport properties of the BSTS solid solutions in a wide range of compositions to determine the more insulating ones. They mapped a composition-structure diagram with a curve (see Fig. 1) showing optimal compositions for insulating behavior near which donors and acceptors almost perfectly compensate each other. Recently many researchers studied bulk crystals with compositions close to this curve [9–16]. The highest resistivity (12.6 Ω cm) and bulk carrier density as low as $2 \times 10^{15} \text{ cm}^{-3}$ were achieved by Pan et al. [15] in a bulk crystal with $x = 0.54$ and $y = 1.2$ at liquid helium temperature. Xu et al. [16] have grown BiSbTeSe_2 bulk crystal with resistivity about 0.5 Ω cm at room temperature. At temperature of 2 K bulk carrier density was lower than $1.4 \times 10^{15} \text{ cm}^{-3}$, the resistivity of the exfoliated flakes varied from 0.04 Ω cm to 4 Ω cm when the device thickness varied from 160 nm to 37 μm. They have observed a well-developed QHE arising from TSS.

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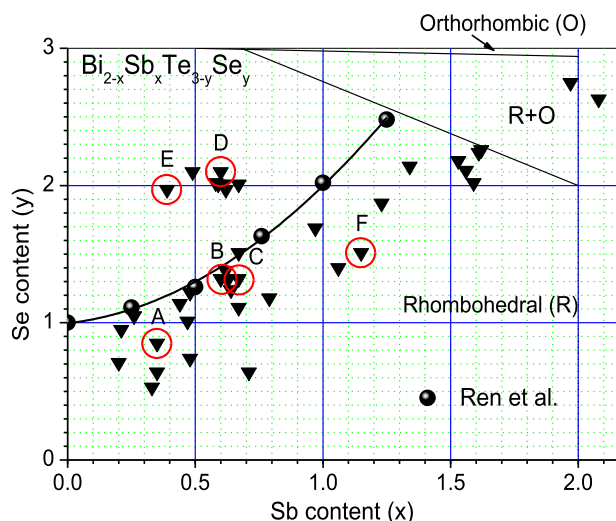


Fig. 1. The composition-structure diagram of BSTS with a map of the grown film compositions (full triangles). The films, transport properties of which were studied, are shown by circles (red online). The full circles show the compositions of bulk crystals with “optimal” insulating behavior determined in Ref. [8]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

To reduce the contribution of bulk carriers into the total transport and to observe surface-dominated transport thin epitaxial films are desirable. To date, MBE and MOVPE technologies for growing BSTS films have not yet been developed. There are only the papers of Tu et al. [17,18] where BSTS films were grown by a catalyst-free physical vapor deposition.

In this paper we report on the MOVPE growth of films of BSTS on sapphire substrates with thin ZnTe buffer layers grown in a single growth run with BSTS. The main task of this work was to determine the dependence of the composition, the surface and the crystal quality of the films on the composition of the vapor phase. Our previous experience on deposition of binary Bi_2Te_3 [19], Sb_2Te_3 [20], Bi_2Se_3 [21] and ternary $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ [22], $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Se}_3$ [23] compounds allowed us to choose appropriate growth conditions to deposit BSTS films with tetradymite structure and V_2VI_3 stoichiometry. To avoid the deposition of phases with other stoichiometries we conducted the growth of BSTS films at a high enough temperature of 445 °C and about 10-fold excess of chalcogen in the vapor phase. We have grown a large series of fairly thick (300–900 nm) films from different compositions of the vapor phase. Thick films were necessary to improve the accuracy of EDX analysis of the films. The results of EDX investigation enable us to grow films of a given composition. The surfaces of the samples were studied by SEM and AFM microscopy. Magnetotransport characterization was carried out for a number of samples.

2. Experimental

Rhombohedral $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ films of various compositions were grown on (0001) Al_2O_3 substrates at a temperature of 445 °C in a horizontal quartz reactor at atmospheric pressure of hydrogen, changing the mole fractions of VI and V precursors in the vapor phase. We used epitaxially (0001) sapphire substrates fabricated by “MONOCRYSTAL PLC” (Russia) without any treatment before the film growth.

First a thin (15 nm) ZnTe buffer layer was deposited on the 2 cm × 2 cm substrate to suppress the dangling bonds of the substrate and to reduce the lattice mismatch [19–23]. The lattice mismatches between ZnTe and sapphire is equal to +10.4%. Of course,

the ZnTe film with thickness of 15 nm is completely relaxed, as it is evidenced by the position of the reflections (111) and (222) in the diffractograms. The lattice mismatches between the binary compounds Bi_2Te_3 , Sb_2Te_3 , Bi_2Se_3 and sapphire are equal to +8.7%, +11.8% and +15.0%, respectively. The lattice mismatches between the relaxed ZnTe layers and the binary compounds listed above are much smaller and are equal to −1.6%, +1.2% and +4.1%, respectively. It is obvious that ZnTe buffer layers are ideally suited for some compositions of BSTS films.

Following growth of the ZnTe buffer layer, after 30 s interruption, all precursors for the growth of BSTS films were simultaneously supplied into the reactor. Trimethylbismuth (BiMe_3), trimethylantimony (SbMe_3), diethylzinc (ZnEt_2), diethyltelluride (TeEt_2) and diisopropylselenide (iPr_2Se) were used, respectively, as bismuth, antimony, zinc, tellurium and selenium organometallic sources whose purities were certified by suppliers as “electronic grade”. BiMe_3 , SbMe_3 , ZnEt_2 , TeEt_2 and iPr_2Se bubblers were held at 0 °C, −30 °C, 10 °C, 25 °C and 27 °C, respectively. Total hydrogen flow was equal to 1.0 l/min during the deposition of ZnTe buffer layers and 0.5 l/min during the epitaxy of BSTS films. The VI/V ratio in vapor phase was close to 10 and the total partial pressure of $\text{BiMe}_3+\text{SbMe}_3$ was equal to 6×10^{-5} bar.

The surfaces of as-grown films were studied using a SEM (Jeol JSM-6480LV) with a tungsten thermionic cathode and AFM (SmartSPM, AIST-NT). To determine the elemental compositions of the films, we used an EDX spectrometer (X-MaxN) with active area of 50 mm², which was docked with the electron microscope. Analysis was performed with the program INCA, “Oxford Instruments”. To standardize and optimize the profiles of emission lines of characteristic radiation the following standards were used: crystals Bi_2Se_3 (Bi-L α and Se-L α), Sb ($\text{Sb-L}\alpha$), ZnS (Zn-L α), PbTe (Te-L α) and Al_2O_3 (Al-K α and O-K α). Measurement of standards and analysis of the samples were performed under identical conditions at an accelerating voltage of 10 kV, and electron probe current of 1.4 nA. Accumulation time of spectra was set equal to 100 s. The detection thresholds for all the elements analyzed are 0.03–0.05 weight%. The composition was measured at 5 or more points for each sample. The dispersions of measured values of weight% for Bi, Sb, Te and Se were equal to 0.16, 0.12, 0.17 and 0.08, respectively. The film thicknesses were determined using AFM by means of a scratch. The Van der Pauw Hall effect technique was applied to evaluate the samples resistivity, mobility and carrier concentration in the range of temperatures 10–300 K. Point ohmic contacts were made by using silver paste. Magnetotransport measurements were carried out in magnetic field up to 1.0 T.

3. Results of growth, EDX, SEM and AFM study of the films

In all growth runs, unless specified otherwise, the duration of BSTS film growth was 1000–2000 s, so that a film thickness, depending on precursors supply, amounted to 300–900 nm. A large thickness of the films is required to exclude the influence of the substrate and the buffer layer on the results of the EDX analysis. X-ray diffraction spectra of BSTS films show the (111) reflection of ZnTe buffer layer, the (0006) reflection of Al_2O_3 substrate and the (00*l*) reflections (*l* = 3, 6, 9, 12, 15, 18) of the rhombohedral phase with V_2VI_3 stoichiometry. For most of the grown samples the FWHMs of (006) rocking curves reflection peaks were lower than 0.2 degrees. This is comparable to the FWHM of the rocking curves for films of bismuth and antimony chalcogenides of binary and ternary compositions grown on sapphire [19,21,23]. Unfortunately, it is impossible to determine the composition quaternary solid solutions solely from diffraction spectra. Table 1 shows the EDX data for 34 samples of BSTS films. The contents of elements Bi, Sb, Te and Se for most samples are close to $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$

Table 1
Results of EDX spectroscopy of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ films.

Sample code	EDS results, $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$				Stoichiometry		$\text{Se}/(\text{Se} + \text{Te})$		$\text{Sb}/(\text{Sb} + \text{Bi})$	
	Bi	Sb	Te	Se	Bi + Sb	Te + Se	Vapor	Solid	Vapor	Solid
T22	1.33	0.67	1.89	1.11	2.0	3.0	0.43	0.37	0.31	0.33
T23	1.52	0.48	2.26	0.74	2.0	3.0	0.30	0.25	0.20	0.24
T25	1.67	0.33	2.47	0.53	2.0	3.0	0.27	0.18	0.15	0.16
T26	1.73	0.26	1.96	1.05	1.99	3.01	0.38	0.35	0.13	0.13
T27	1.53	0.48	1.77	1.22	2.01	2.99	0.44	0.41	0.25	0.24
T28(A) ^a	1.65	0.35	2.15	0.85	2.0	3.0	0.350	0.28	0.17	0.17
T29	1.55	0.47	1.97	1.01	2.02	2.98	0.44	0.34	0.22	0.23
T31	1.79	0.21	2.05	0.95	2.0	3.0	0.415	0.32	0.14	0.11
T32	1.58	0.44	1.84	1.14	2.02	2.98	0.467	0.38	0.29	0.22
T33(B) ^a	1.43	0.60	1.65	1.32	2.03	2.97	0.50	0.44	0.33	0.30
T34(C) ^a	1.36	0.67	1.65	1.32	2.03	2.97	0.50	0.44	0.38	0.33
T37	1.24	0.79	1.79	1.18	2.03	2.97	0.541	0.40	0.489	0.39
T38	0.97	1.06	1.57	1.4	2.03	2.97	0.527	0.471	0.568	0.52
T39(F)	0.89	1.15	1.45	1.51	2.04	2.96	0.63	0.51	0.68	0.56
T41	1.31	0.71	2.34	0.64	2.02	2.98	0.30	0.23	0.38	0.35
T42	1.80	0.20	2.29	0.71	2.0	3.0	0.30	0.24	0.12	0.10
T43	1.06	0.97	1.28	1.69	2.03	2.97	0.58	0.52	0.56	0.48
T68	0.80	1.23	1.10	1.87	2.03	2.97	0.70	0.63	0.66	0.61
T70	0.69	1.34	0.83	2.14	2.03	2.97	0.81	0.71	0.71	0.66
T71	0.51	1.53	0.77	2.18	2.03	2.97	0.82	0.73	0.82	0.75
T72 ^b	0.44	1.61	0.71	2.24	2.05	2.95	0.88	0.70(R)	0.84	0.79(R)
T73 ^b	0.16	1.97	0.12	2.75	2.13	2.87	0.88	0.92(O)	0.84	0.96(O)
	0.42	1.62	0.7	2.26	2.04	2.96	0.85	0.76(R)	0.842	0.79(R)
	0.16	2.08	0.13	2.63	2.24	2.76	0.85	0.95(O)	0.842	0.93(O)
T74	0.48	1.56	0.85	2.11	2.04	2.96	0.807	0.71	0.829	0.76b
T75	0.46	1.59	0.93	2.02	2.05	2.95	0.763	0.69	0.83	0.78b
T76	1.37	0.64	1.75	1.24	2.01	2.99	0.370	0.41	0.457	0.32
T77	1.43	0.58	1.53	1.45	2.02	2.98	0.545	0.483	0.442	0.29
T78	1.35	0.67	0.68	2.31	2.01	2.99	0.758	0.763	0.377	0.33
T79	1.40	0.61	0.89	2.10	2.01	2.99	0.703	0.70	0.351	0.305
T80	1.43	0.59	1.04	1.95	2.01	2.99	0.767	0.65	0.237	0.295
T81	1.52	0.49	0.89	2.10	2.01	2.99	0.765	0.70	0.243	0.245
T82(E) ^a	1.62	0.39	1.03	1.97	2.00	3.00	0.736	0.66	0.234	0.21
T83	1.41	0.62	1.00	1.97	2.03	2.97	0.730	0.657	0.257	0.31
T84(D) ^a	1.42	0.60	0.88	2.10	2.02	2.98	0.722	0.70	0.354	0.30
T85	1.65	0.35	2.36	0.64	2.00	3.00	0.385	0.213	0.151	0.175

The orthorhombic phase does not fit the stoichiometry of V_2VI_3 composition.

^a These samples are named by alphabetic symbols in Fig. 1 and in transport part of the paper.

^b Biphasic samples, the results are given for the rhombohedral (R) and orthorhombic (O) phases.

formula. This is confirmed by the columns “Stoichiometry” in Table 1. The exceptions are samples T72 and T73 with high contents of antimony and selenium. These films include both rhombohedral and orthorhombic phases. The compositions of all the samples listed in Table 1 are shown in the composition-structure

diagram of the $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ system together with the curve of Ren et al. [8], see Fig. 1.

In Table 1, the right-hand columns give the values of mole fractions of selenium and antimony in the vapor and solid phases. Fig. 2a shows the $\text{Sb}/(\text{Sb} + \text{Bi})$ ratio in BSTS films versus mole

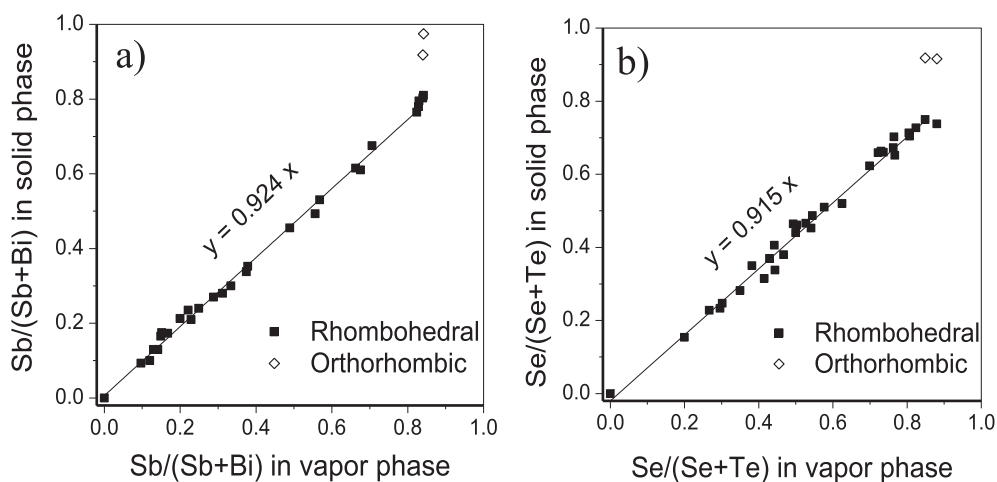


Fig. 2. The relationships between the mole fractions of Sb (a) and Se (b) in vapor and solid phases.

fraction of SbMe_3 in the total flux of V-group precursors at the inlet to the reactor. Fig. 2b shows that dependence for the selenium component. Both dependencies in Fig. 2 have a linear character with coefficients close to 1, thus we were able to get films of desired compositions. It should be noted that the compositions of the films grown on a nonrotating substrate are quite homogeneous along the direction of gas flow, see Fig. 3.

It is believed that the deposition of bismuth and antimony chalcogenides films proceeds as van der Waals epitaxy, and it is possible to grow them on substrates with large lattice mismatch. The ZnTe buffer layer significantly reduces the mismatch between substrate and BSTS lattices. Nevertheless, we have observed the coherent 3D islands on the surfaces of films with 10–60 nm thickness. Thus, at an initial stage the BSTS deposition proceeds in 3D Stranski-Krastanov growth mode as earlier observed for MOVPE growth of Bi_2Se_3 , Bi_2Te_3 and Sb_2Te_3 films [19–21].

Fig. 4a) shows the AFM image of $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$ of the film T24 (not shown in Table 1) with $\text{Bi}_{1.85}\text{Sb}_{0.15}\text{Te}_{2.02}\text{Se}_{0.98}$ composition and average thickness of 35 nm. This film is not compact and the holes down to buffer ZnTe layer occupy about 15% of the area of the scan. Fig. 4d), where a surface profile of the film along the straight line depicted in Fig. 4a) is given, demonstrates this. As a rule, when the average film thickness reaches about 60 nm, further growth follows essentially in 2D Frank-van der Merwe growth mode. So, for most BSTS films given in Table 1 the rms over an area of $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$ was less than 1 nm. In Fig. 4(b), (c), (g) the AFM images over areas of $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$ are shown for films T84 (thickness $d = 900\text{ nm}$, $\text{rms} = 0.57\text{ nm}$), T28 ($d = 310\text{ nm}$, $\text{rms} = 0.91\text{ nm}$) and T33 ($d = 620\text{ nm}$, $\text{rms} = 0.49\text{ nm}$). The wide flat terraces and long steps are well visible in these images. The height of each step is about 1 nm, as seen in the surface profile for the T84 sample in Fig. 4(e), and this is consistent with the thickness of one quintuple layer. On the terraces of the T84 sample there are also defects in the form of small dark spots, see Fig. 4(b). The surface profile along the straight line passing through two such defects, Fig. 4(e), indicates that they are deep pits, apparently formed by dislocations in the BSTS film. Similar defects were found on one third of the samples presented in Table 1. On the scan of sample T28 in addition to four dark spots there are also four light-colored spots. The surface profile in Fig. 4f) clearly demonstrates that the light-colored spots are hillocks. The hillocks were found only on a few samples of BSTS films given in Table 1. Fig. 4(h) shows a 3D AFM image of $4.8\text{ }\mu\text{m} \times 4.8\text{ }\mu\text{m}$ surface area of the T28 sample. The densities of the hillocks and pits are equal to $6 \times 10^7\text{ cm}^{-2}$ and $1.3 \times 10^8\text{ cm}^{-2}$, respectively. Since the hillocks are slim and high their

faceting in AFM images are distorted. In reality they are not conical, as is seen in the SE micrograph of sample T39 ($x = 1.15$, $y = 1.51$) in Fig. 4l). We suppose that the hillocks are formed as a result of a segregation of excess chalcogens to the surface of the grown film during its cooling. This is similar to the formation of Se hillocks on the surface of ZnSe films grown by the MOVPE method [24]. Unfortunately, the small size of precipitates does not allow us to determine their composition by EDX spectroscopy.

In SEM micrographs of thick BSTS films with composition not close to the two-phase R + O area in the composition-structure diagram of Fig. 1, there are practically no visible defects, see Fig. 4(j). We rarely found large growth figures in the form of trihedral truncated pyramids on a smooth enough surface, see Fig. 4(k). Upon increasing the content of antimony and selenium in films, the surfaces of thick films become embossed, the films formation take place in mixed 2D–3D growth modes. The surface of one such film (T71, $x = 1.53$, $y = 2.18$) is shown in Fig. 4(m). Further increase of antimony content in the films leads to a two-phase area in the composition-structure diagram in Fig. 1. Precipitates of the orthorhombic phase were found in the samples T73 ($x = 1.62$, $y = 2.26$) and T72 ($x = 1.61$, $y = 2.24$). Usually the precipitates are small and occupy no more than 1–2% of the area of these films. However, one can also see large conglomerates such as those shown in Figs. 4(n) and (o). In the vicinity of such conglomerates, the 2D growth mode of the rhombohedral phase is violated and cracks appear in the film. It should be noted that in ternary $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ films at $x \sim 0.25$ cracking and discontinuity of the coating were also observed, moreover at large value of x nanosheets of orthorhombic phase were formed [23].

4. Electrical transport characterization

Transport properties of a number of the grown films were studied using van der Pauw Hall effect measurements in the range of temperatures 10–300 K. The technological parameters and some transport characteristics of the tested films are given in Table 2. Fig. 5(a)–(c) show the temperature dependencies of the films' resistivities. Except for the films E ($x = 0.39$, $y = 1.97$) and D ($x = 0.6$, $y = 2.1$) with high Se content, the overall temperature dependencies of the films' resistivities are similar: with decreasing temperature the resistivity increases, then saturates. The resistivity of the sample E is almost independent of temperature in the range of measurement temperatures. The resistivity of the film D increases with decreasing temperature in the range of temperatures 300–200 K; very slightly depends on temperature in the range of temperatures 200–100 K and noticeably decreases with the further decrease of temperature below 100 K (see upper curve in Fig. 5(a)). Usually the increase of TI resistivity with decreasing temperature is described by an activated behavior $\rho \propto \exp(\Delta/k_B T)$, where Δ is an activation energy [3,15]. Such behavior is supposed to result from a fluctuating potential profile in heavily compensated semiconductor and the presence of charge puddles [25,26]. We plot in Fig. 5(b) $\ln \rho$ versus $1/T$ and determine the values of Δ which are close to those in Refs. [3,15], but the range of activation behavior is very narrow in particular for the samples D and F. In the range of temperatures 50–250 K the temperature variation of the resistivity looks more convincing in a plot of $\ln \rho$ versus $T^{-1/4}$, Fig. 5(c). At temperatures below 50 K the resistivity saturated and for some samples even decreased with decreasing temperature. This indicates that the film's conductivity can be described by parallel conductivities of the insulating bulk and the metallic surface states, the role of surface states becoming prevalent at lower temperatures.

The magnetoresistivities $\Delta R_{\text{bd,ac}}$ of three samples measured at different temperatures are shown in Fig. 5(d), (e) and (f). The

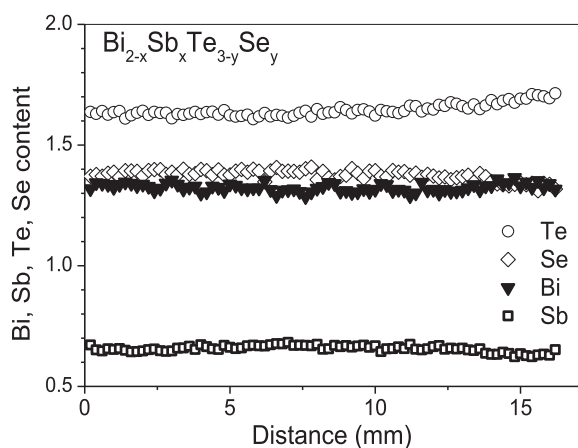


Fig. 3. Distributions of Bi, Sb, Te and Se in the T34 film along the gas flow direction. The content of elements is presented in units of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ formula. During the growth run the sapphire substrate was not rotated.

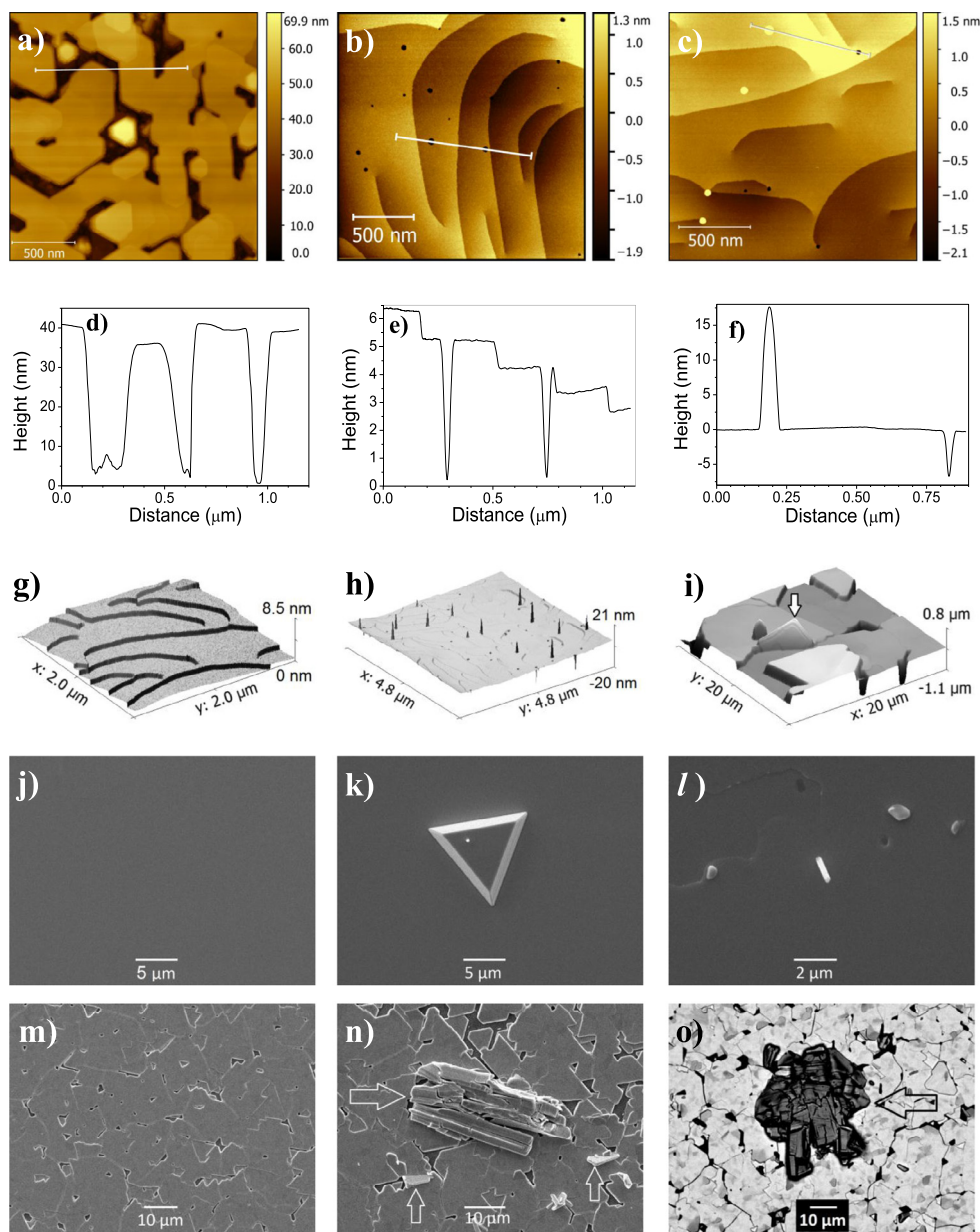


Fig. 4. 2D AFM images (2 $\mu\text{m} \times 2 \mu\text{m}$) of T24 (a), T84 (b) and T28 (c) films. The films thicknesses and the values of the rms are 35, 900, 520 nm and 5.9, 0.57, 0.91 nm, respectively; Surface profiles of T24 (d), T84 (e) and T28 (f) samples along lines shown in a, b and c respectively; 3D AFM images of T33 (g), T28 (h) and T72 (i) films; SEM micrographs of T43 (j), T37 (k), T39 (l), T71 (m), T73 (n) and T72 (o) films. Arrows in (i), (n), (o) indicate the precipitates of the orthorhombic phase.

Table 2
Transport properties of the $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ films.

Sample code	Thickness, nm	$\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$		Carrier type		Δ (meV)	$n_{\text{eff}}(300/10 \text{ K})$ (10^{18} cm^{-3})	μ (300/10 K) (cm^2/Vs)	ρ (300/10 K) $\Omega \text{ cm} \times 100$
		x	y	n	p				
A	310	0.35	0.85	<50 K	>50 K	20	20/1.4	60/73.6	0.84/59
B	610	0.6	1.32	<170 K	>170 K	52	7.8/0.29	45/174.5	1.46/15
C	620	0.67	1.32	<150 K	>150 K	56	10/0.20	39/209.4	1.27/18
D	900	0.6	2.10	10–300		75	6.7/0.22	110/139.5	4.65/20
E	500	0.39	1.97	10–300			1.6/0.93	170/140	2.3/4.8
F	750	1.15	1.5		10–300	21	17/1.25	90/76	0.27/4.2

nonlinear dependencies of low temperature magnetoresistivity on magnetic field also evidence the presence of more than one conductive channel. As expected, the films D and E with high content of selenium, whose compositions in the diagram of Fig. 1 lie well

above the Ren curve, possess conductivity of n-type in the whole range of temperatures 10–300 K. This is confirmed by the slope of the entire series of curves $\Delta R_{\text{bd},ac}$ versus the magnetic field strength Fig. 5(d). The film F with the highest antimony content

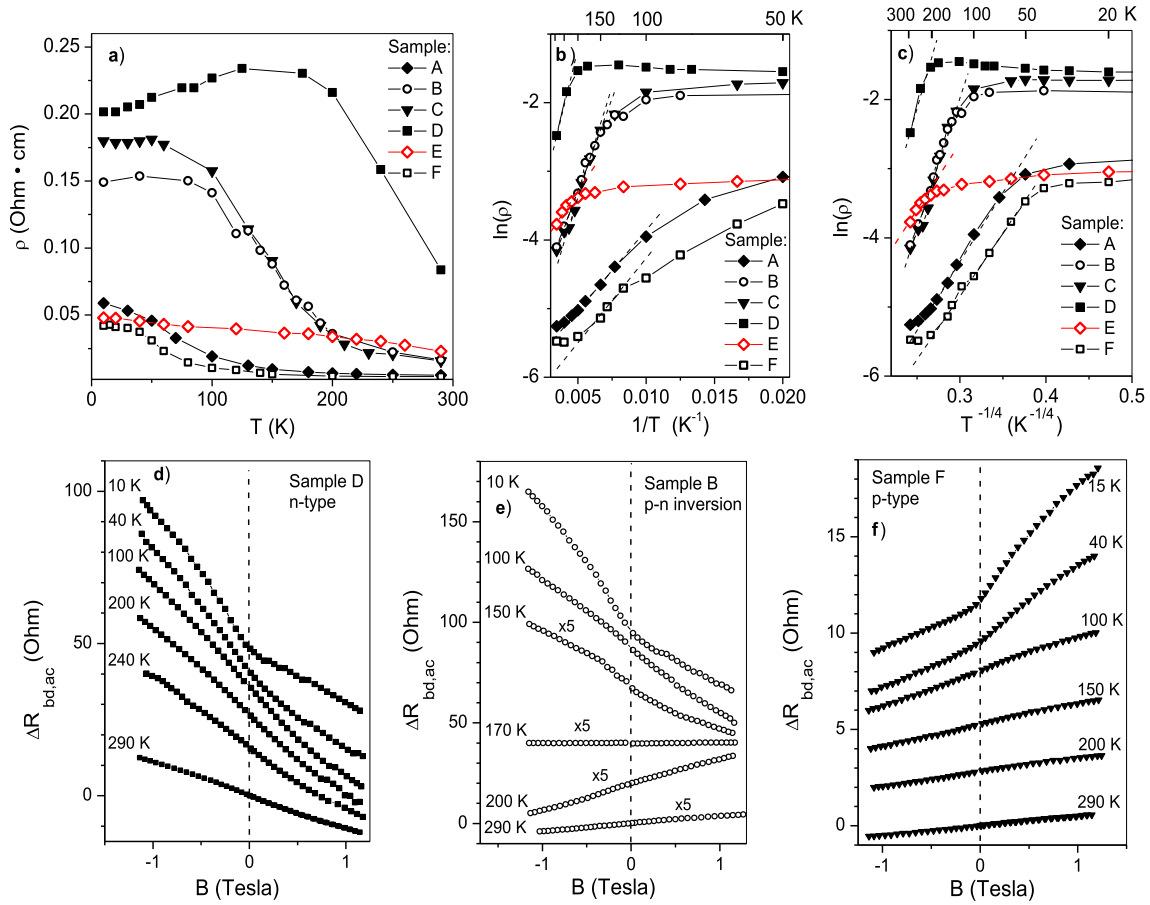


Fig. 5. Temperature dependencies of the six films' resistivities ρ (a); the Arrhenius plot of ρ (b); plot of ρ vs $T^{-1/4}$ (c), (curves for sample E red online); magnetoresistivity $\Delta R_{bd,ac}$ measured at different temperatures vs magnetic field for samples D (d), B (e) and F (f). Curves in d, e, f are shifted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

($x = 1.15$, $y = 1.5$) has a conductivity of p-type in the whole range of temperatures. Three other samples A, B and C have p-type conductivity at 300 K, but with decreasing temperature the conductivity changes from p-type to n-type. For the sample B, for example, the inversion occurs at a temperature of 170 K, as it is seen from the series of curves shown in Fig. 5(e). The change of $\Delta R_{bd,ac}$ sign with lowering temperature may be understood as a result of the presence of two parallel channels: bulk hole conductance prevailing at higher temperatures and surface states electron conductance dominating at lower temperatures. This scenario is possible in TI with Dirac point near the valence band edge. The change of conductivity type with temperature can also happen if there are two types of bulk defects, one n-, the other p-type, with different activation energies and different concentrations.

The transport characteristics of the films B and C with similar thickness and composition are close in values (see Fig. 5(a), (b) and Table 2), which indicates good reproducibility of the BSTS films deposition technology. Note that the resistivities of our samples are more than an order of magnitude lower than those in Ref. [15], where the resistivity of samples decreases from 15 Ω cm to 2.5 Ω cm with decreasing sample thicknesses from 100 μ m to 6 μ m. We suppose that the lower resistivity results from the lower thickness of our samples: the contribution of metallic surface states with high conductivity is larger than in thick films. The larger carrier concentration than those in Refs. [3,15] may also result from parallel channels of the insulating bulk and the metallic TSS. The resistivities in Fig. 5a) are close to those of Ref. [16], where the resistivity of the flake of thickness 450 nm was about 0.04 Ω cm and 0.2 Ω cm at 290 K and 2 K respectively. But all samples in

Fig. 5 have different compositions, which are other than in the paper by Xu et al. and we cannot compare them quantitatively.

The results obtained in the present study indicate a significantly lower concentration of bulk carriers in the films of quaternary composition in comparison with their concentration in our binary and ternary composition films. Our best result for carrier concentration in a thick 750 nm Bi_2Se_3 film was $2 \times 10^{18} \text{ cm}^{-3}$ at 300 K and $1.52 \times 10^{18} \text{ cm}^{-3}$ at 10 K, for ternary $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ the results were much worse. As seen from Table 2, in the films B, C, D of the quaternary compositions of comparable thickness, the low temperature carrier concentrations are an order of magnitude lower.

5. Discussion and conclusion

Epitaxial films of rhombohedral $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ over a wide range of composition were grown on Al_2O_3 (0001) substrates with thin ZnTe buffer layers for the first time. The results of EDX spectroscopy show good compliance of most samples with V_2VI_3 stoichiometry. A linear relationship was found between the mole fractions of antimony $\text{Sb}/(\text{Sb} + \text{Bi})$ and selenium $\text{Se}/(\text{Se} + \text{Te})$ in the solid phase and at the inlet to the reactor, which allows us to readily grow BSTS film with a given composition. At the initial stage of BSTS deposition the 3D growth mode was observed; when a film thickness reaches 60 nm the 2D growth mode predominated. For most BSTS films listed in the Table 1 the value of rms over an $2 \mu\text{m} \times 2 \mu\text{m}$ surface area was less than 1 nm. According to SEM

study, the formation of rhombohedral films with high antimony and selenium contents occurs in mixed 2D–3D growth modes.

Transport characterization of the grown films were carried out. High temperature dependencies of the resistivity can be fitted better by $\rho \propto T^{-1/4}$ other than activation behavior. There are also samples with almost temperature independent resistivity. The resistivity of some samples decreases with decreasing temperature below 50 K. These dependencies and the nonlinear dependence of magnetoresistivities $\Delta R_{bd,ac}$ on magnetic field evidence the presence of the conductive channel additional to bulk conductivity. We suppose that this is a manifestation of the conductivity of TSS. A study of $\Delta R_{bd,ac}$ shows that films above the Ren curve have n-type conductivity, lower ones have p-type, and films with a composition near this curve change the type of conductivity from p- to n-type when the temperature decreases. Further improving the quality of films, including usage of more suitable substrates such as (111) GaAs, and studying transport properties of the films with optimized compositions is our immediate task. To reveal the role of TSS in transport additional transport measurements are required. We plan to study magnetotransport in higher magnetic fields and the film resistivity dependence of their thickness.

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References

- [1] M.Z. Hasan, C.L. Kane, Rev. Mod. Phys. 82 (2010) 3045, <https://doi.org/10.1103/RevModPhys.82.3045>.
- [2] T. Arakane, T. Sato, S. Souma, K. Kosaka, K. Nakayama, M. Komatsu, T. Takahashi, Z. Ren, K. Segawa, Y. Ando, Nat. Com. 3 (2012) 636, <https://doi.org/10.1038/ncomms1639>.
- [3] Z. Ren, A.A. Taskin, S. Sasaki, K. Segawa, Y. Ando, Phys. Rev. B 82 (2010) 241306, <https://doi.org/10.1103/PhysRevB.82.241306>.
- [4] A.A. Taskin, H.F. Legg, F. Yang, S. Sasaki, Y. Kanai, K. Matsumoto, A. Rosch, Y. Ando, 2017, Also available at: [arXiv:1703.03406v1](https://arxiv.org/pdf/1703.03406v1) [cond-mat.mes-hall], <https://arxiv.org/pdf/1703.03406.pdf>.
- [5] Y. Tung, Y.F. Chiang, C.W. Chong, Z.X. Deng, Y.C. Chen, J.C.A. Huang, C.-M. Cheng, T.-W. Pi, K.-D. Tsuei, Z. Li, H. Qiu, J. Appl. Phys. 119 (2016) 055303, <https://doi.org/10.1063/1.4941018>.
- [6] W. Zou, W. Wang, X. Kou, M. Lang, Y. Fan, E.S. Choi, A.V. Fedorov, K. Wang, L. He, Y. Xu, K.L. Wang, Appl. Phys. Lett. 110 (2017) 212401, <https://doi.org/10.1063/1.4983684>.
- [7] I. Teramoto, S. Takayanagi, J. Phys. Chem. Solids 19 (1961) 124, [https://doi.org/10.1016/0022-3697\(61\)90065-8](https://doi.org/10.1016/0022-3697(61)90065-8).
- [8] Z. Ren, A.A. Taskin, S. Sasaki, K. Segawa, Y. Ando, Phys. Rev. B 84 (2011) 165311, <https://doi.org/10.1103/PhysRevB.84.165311>.
- [9] W. Ko, I. Jeon, H.W. Kim, H. Kwon, S.-J. Kahng, J. Park, J.S. Kim, S.W. Hwang, H. Suh, Sci. Rep. 3 (2013) 2656, <https://doi.org/10.1038/srep02656>.
- [10] J. Lee, J. Park, J.-H. Lee, J.S. Kim, H.-J. Lee, Phys. Rev. B 86 (2012) 245321, <https://doi.org/10.1103/PhysRevB.86.245321>.
- [11] S. Kim, S. Yoshizawa, Y. Ishida, K. Eto, K. Segawa, Y. Ando, S. Shin, F. Komori, Phys. Rev. Lett. 112 (2014) 136802, <https://doi.org/10.1103/PhysRevLett.112.136802>.
- [12] P. Dutta, A. Pariari, P. Mandal, Sci. Rep. 7 (2017) 4883, <https://doi.org/10.1038/s41598-017-05164-9>.
- [13] W. Wang, L. Li, W. Zou, L. He, F. Song, R. Zhang, X. Wu, F. Zhang, Sci. Rep. 5 (2015) 7931, <https://www.nature.com/articles/srep07931.pdf>.
- [14] T.C. Hsiung, C.Y. Mou, T.K. Lee, Y.Y. Chen, Nanoscale 00 (2014) 1, <https://doi.org/10.1039/C4NR05376A>.
- [15] Y. Pan, D. Wu, J.R. Angevaere, H. Luigjes, E. Frantzeskakis, N. de Jong, E. van Heumen, T.V. Bay, B. Zwartsenberg, Y.K. Huang, M. Snelder, A. Brinkman, M.S. Golden, A. de Visser, New J. Phys. 16 (2014) 123035, <https://doi.org/10.1088/1367-2630/16/12/123035>.
- [16] Y. Xu, I. Miotkowski, C. Liu, J. Tian, H. Nam, N. Alidoust, J. Hu, C.-K. Shih, M.Z. Hasan, Y.P. Chen, Observation of topological surface state quantum hall effect in an intrinsic three-dimensional topological insulator, Nat. Phys. 10 (2014) 956, <https://doi.org/10.1038/NPHYS3140>.
- [17] N.H. Tu, Y. Tanabe, K.K. Huynh, Y. Sato, H. Oguro, S. Heguri, K. Tsuda, M. Terauchi, K. Watanabe, K. Tanigaki, Appl. Phys. Lett. 105 (2014) 063104, <https://doi.org/10.1063/1.4892576>.
- [18] N.H. Tu, Y. Tanabe, Y. Satake, K.K. Huynh, P.H. Le, S.Y. Matsushita, K. Tanigaki, Nano Lett. 17 (2017) 2354, <https://doi.org/10.1021/acs.nanolett.6b05260>.
- [19] P.I. Kuznetsov, V.O. Yapaskurt, B.S. Shchamkhalova, V.D. Shcherbakov, G.G. Yakushcheva, V.A. Luzanov, V.A. Jitov, J. Cryst. Growth 455 (2016) 122, <https://doi.org/10.1016/j.jcrysgro.2016.09.055>.
- [20] P.I. Kuznetsov, B.S. Shchamkhalova, V.O. Yapaskurt, V.D. Shcherbakov, V.A. Luzanov, G.G. Yakushcheva, V.A. Jitov, V.E. Sizov, J. Cryst. Growth 471 (2017) 1, <https://doi.org/10.1016/j.jcrysgro.2017.05.002>.
- [21] P.I. Kuznetsov, V.A. Luzanov, G.G. Yakushcheva, A.G. Temiryazev, B.S. Shchamkhalova, V.A. Zhitov, L.Yu. Zakharov, J. Com. Technol. Electron. 61 (2016) 183, <https://doi.org/10.1134/S1064226916010083>.
- [22] P.I. Kuznetsov, G.G. Yakushcheva, V.A. Luzanov, A.G. Temiryazev, B.S. Shchamkhalova, V.A. Jitov, V.E. Sizov, J. Cryst. Growth 409 (2015) 56, <https://doi.org/10.1016/j.jcrysgro.2014.09.035>.
- [23] P.I. Kuznetsov, V.O. Yapaskurt, B.S. Shchamkhalova, V.D. Shcherbakov, G.G. Yakushcheva, V.A. Luzanov, V.A. Jitov, J. Cryst. Growth 433 (2016) 114, <https://doi.org/10.1016/j.jcrysgro.2015.10.006>.
- [24] V. Kozlovsky, V. Krivobok, S. Nikolaev, E. Onishchenko, A. Pruchkina, P. Kuznetsov, V. Zhitov, J. Russ. Laser Res. 37 (2016) 273, <https://doi.org/10.1007/s10946-016-9571-y>.
- [25] T. Knispel, W. Jolie, N. Borgwardt, J. Lux, Z. Wang, Y. Ando, A. Rosch, T. Michely, M. Gruninger, Phys. Rev. B 96 (2017) 195135, <https://doi.org/10.1103/PhysRevB.96.195135>.
- [26] B. Skinner, T. Chen, B.I. Shklovskii, J. Exp. Theo. Phys. 117 (2013) 579, <https://doi.org/10.1134/S1063776113110150>.