MOVPE deposition and optical properties of thin films of a Bi$_2$Te$_{3-x}$Se$_x$ topological insulator

V V Kovalev$^1$, P I Kuznetsov$^1$, G G Yakushcheva$^1$, O V Yapaskurt$^{1,2}$, V I Kovalev$^1$, A I Rukovishnikov$^1$ and S V Kovalev$^1$

$^1$V. A. Kotelnikov Institute of Radio-Engineering and Electronics, Russian Academy of Sciences, 1 B.A. Vvedenskii Sq., Fryazino, Moscow Region 141190, Russia

$^2$Department of Petrology, Lomonosov Moscow State University, Moscow 119991, Russia

E-mail: vladimirkovalev.inc@gmail.com

Abstract. A set of monocrystalline Bi$_2$Te$_{3-x}$Se$_x$ films of various compositions were synthesized by metalorganic vapor epitaxy. The smooth films with thicknesses of about 500 nm were grown on (0001) Al$_2$O$_3$ substrates at 465 °C using trimethylbismuth, diethyltellurium and disopropylselenium as meta-organic precursors. The epitaxial nature of the films and their rhombohedral crystal structure are confirmed by X-ray studies and Raman spectroscopy. The elemental composition of the films was determined by energy dispersive X-ray spectrometry. Optical properties of Bi$_2$Te$_{3-x}$Se$_x$ films were examined in the 260-1000 nm range by multi-angle spectroscopic ellipsometry (SE). It was shown that the optical properties of Bi$_2$Te$_{3-x}$Se$_x$ films vary monotonically depending on the ratio of selenium to tellurium. It is demonstrated that SE can be used for rapid assessment of the composition of Bi$_2$Te$_{3-x}$Se$_x$ films.

1. Introduction

Topological insulators are a new class of narrow band gap semiconducting materials characterized by the presence of strong spin-orbit interactions, which invert the orbital character of conduction and valence bands [1]. Topological insulators behave in the bulk like ordinary insulators, but they additionally support a conducting two-dimensional topological surface state with the linear energy-momentum dispersion shaped like a Dirac cone [2]. Bi$_2$Te$_{3-x}$Se$_x$ compounds that were originally employed for thermolectric devices due to their large Seebeck constant [3] belong to this category because of the large spin-orbit coupling due to heavy bismuth atoms. Chalcogenides of bismuth are narrow-gap semiconductors (bandgap less than 0.3 eV) with a rhombohedral (tetradyomite) crystal structure. The combination of a wide spectral range, a high modulation depth of the absorption coefficient, and resistance to damage by high-intensity light coupled with low fabrication cost make these materials attractive for use as passively Q-switched elements in a fiber laser scheme [4-5].

For practical device applications, epitaxial layers are desired for monolithic integration in multilayers and gated heterostructures that would allow tuning of the Fermi level to the Dirac point and control spin-polarized currents in devices. [6]. The Bi$_2$Se$_3$ films are usually n-type owing to a large amount of Se vacancies [7]. The Bi$_2$Te$_3$ films may be p-type but usually they are highly metallic [8] due to antisite defects which are promoted by close electronegativities of Bi and Te. One of the
ways to modify the surface properties of topological insulators is to change the chemical composition of chalcogenides.

Bi$_2$Te$_{3-x}$Se$_x$ films can be grown by molecular beam epitaxy [9-11] or metal-organic vapour epitaxy [12]. The latter method allows both deposition of thin films of chalcogenides on various flat surfaces (for example, on a sapphire substrate or a fiber end face [5]) and growth of a uniform film on a side-polished and/or tapered surface of a fiber, which cannot be achieved by magnetron sputtering or laser ablation [13-14].

The published experimental and calculated data on the optical properties of Bi$_2$Te$_{3-x}$Se$_x$ thin films are incomplete and contradictory [11, 15, 16]. In this paper, we used multi-angle spectroscopic ellipsometry (SE) to examine optical properties in the 260-1000 nm spectral range of Bi$_2$Te$_{3-x}$Se$_x$ films grown by MOVPE on sapphire substrates.

2. Samples and experimental

Rhombohedral Bi$_2$Te$_{3-x}$Se$_x$ films were grown by MOVPE (metalorganic vapor phase epitaxy) on sapphire (0001) Al$_2$O$_3$ substrates with a thin ZnTe buffer layer in a horizontal quartz reactor at atmospheric pressure of hydrogen. Trimethylbismuth (BiMe$_3$), diethylzinc (ZnEt$_2$), diethyltellurium (Et$_2$Te) and diisopropylselenium (iPro$_2$Se) were used, respectively, as bismuth, zinc, tellurium and selenium organometallic precursors. BiMe$_3$, ZnEt$_2$, Et$_2$Te and iPro$_2$Se bubblers were held at 20 °C, 10 °C, 20 °C and 28 °C, respectively. Thin (15 nm) ZnTe buffer layers were grown in a single process cycle with films of a topological insulator at a temperature of 445 °C. The buffer layer is necessary for passivation of free bonds of a sapphire substrate that prevent the formation of continuous films by the van der Waals mechanism. The Te/Zn ratio in the gas phase was maintained close to unity. Rocking curves of (111) reflection of ZnTe films were below 0.18 degree. Bi$_2$Te$_{3-x}$Se$_x$ films about 0.5 microns thick had a mirror surface. The epitaxial nature of the films and their crystal rhombohedral structure are confirmed by X-ray studies and Raman spectroscopy.

To determine the elemental composition of the films, we used an energy dispersive X-ray spectrometer. The chemical compositions of Bi$_2$Te$_{3-x}$Se$_x$ films were studied using a JEOL JSM-6480LV (JEOL, Japan) scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Department of Petrology, Moscow State University). To standardize and optimize the profiles of emission lines of characteristic radiation, the following standards were used: crystal Bi$_2$Se$_3$ (Bi-M$\alpha$ and Se-L$\alpha$), PbTe (Te-L$\alpha$) and ZnS (Zn-L$\alpha$). The measurement of standards and analysis of samples were performed under identical conditions: an acceleration voltage of 10 kV, a beam current of 1.4 nA, and an accumulation time for spectra of 100 seconds. The detection thresholds for all the elements analyzed are 0.03 - 0.05 weight %. The measurements of each sample were carried out at least in 5 points.

![Figure 1. ES-2LED Variable Angle Spectroscopic Ellipsometer.](image)
The optical properties of the samples were studied by the SE method at angles of incidence of 60, 65, and 70 degrees in the spectral range of 260 – 1000 nm. The measurements were carried out on an “ES-2LED” installation, which is a LED spectral ellipsometer [17] that allows taking magneto-optical measurements [18]. Figure 1 shows the measurement setup. An achromatic compensator was used to improve the metrological characteristics of the spectroellipsometer [19-20]. The measurement reproducibility and stability of the ellipsometric parameters $\Psi$ and $\Delta$ are no worse than 0.001 and 0.01°, respectively. The reproducibility of the $\Psi$ and $\Delta$ measurements of metal films at the peak wavelengths of the LED radiation is around 0.0003 and 0.001°, respectively. The spectral resolution is 4 nm. The minimum time to measure $\Psi$ and $\Delta$ in the entire wavelength range is 20 s.

3. Results and discussion

X-Ray study showed that the lattice parameter c of rhombohedral Bi$_2$Te$_{3-x}$Se$_x$ films vary almost linearly with increasing $x$. Only the lines corresponding to (00$l$) with $l$ = 3; 6; 9; 12; 15 and 18 planes of films and the 006 line of sapphire substrates were observed in XRD spectra. This indicates that we obtained the single crystalline films with the c axis perpendicular to the (0001) plane of sapphire.

Optical properties are used to characterize the optoelectronic behavior of any condensed-matter systems for technical applications. Therefore, it is essential to use a reliable approach to accurately describe these properties in agreement with experimental findings.

Spectroscopic ellipsometry is one of the most adapted optical techniques to analyze solid surfaces, interfaces and buried layers, because it is a non-invasive optical method and needs no reference samples for calibration. SE measures the changes in light polarization which occur upon reflection from a sample surface as a function of the light wavelength. This change can be described by ellipsometric angles $\Psi$ and $\Delta$, which are the amplitude and phase of the complex reflectance ratio

$$\rho = \frac{r_p}{r_s} = \frac{\tan \Psi}{\exp(i\Delta)}.$$ \hspace{1cm} (1)

where the parameters $r_p$ and $r_s$ are the complex reflection coefficients for parallel and perpendicular light polarizations, respectively. SE, as an express method for the analysis of thin films, has a number of characteristic features that make it a widely used measurement method in the semiconductor industry. The measured spectra of ellipsometric parameters characterize the surface and transition layers of the material, including surface roughness, thickness, electronic and optical properties.

The SE method with the binary polarization modulation conditions [21] has been used here, since it has several advantages compared with the rotating polarizer SE. The key element of our system is a polarization switcher which transforms the unpolarized light from a source into highly linearly polarized light with alternate and orthogonal polarizations. The polarization switcher does not contain any moving optical element, which provides high precision due to the absence of any mechanical vibrations and wobbling in the optical track and the binary polarization modulation. The simultaneous acquisition allows one to increase the signal-to-noise ratio even with the unstable radiation sources [22]. Using a proper model for the layered structure, the real and imaginary parts of the dielectric function can be determined by SE measurements without using the Kramers-Kronig relations.

Multiple-angle measurements of the spectra of ellipsometric parameters significantly increase the reliability of measurements in the case of complex structures with initially unknown optical properties. Figure 2 shows the measured spectral dependence of ellipsometric angles $\Psi$ and $\Delta$ of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ films of a 490 nm thickness, deposited on sapphire substrates, in the wavelength range of 260 – 1000 nm at 60, 65 and 70 incidence angles. At such thicknesses, the Bi$_2$Te$_{1-x}$Se$_x$ films are completely opaque, which makes it possible to use a two-layer (film/surface layer) model for determining its optical properties from SE spectra.

A surface layer on the top of the films was assumed to fit the measured ellipsometric spectra. We have found that $rms$ of AFM scans on a 10 x 10 $\mu$m$^2$ area has a strong dependence on the film thickness. For example, $rms$ of a film with a thickness of 30 nm was several times higher than that for a film with a thickness of 110 nm. This is because of the growth mode conversion (3D→2D) with increasing film thickness. As a result, when the thickness reached 500 nm, $rms$ was 1-2 nm.
Figure 2. SE spectra for MOVPE Bi$_2$Te$_{3-x}$Se$_x$ films, (a) – $x$ = 3, (b) – $x$ = 0. Circles (1), up triangles (2) and down triangles (3) are the SE spectra for the incident angles of 60°, 65° and 70°, respectively.

The AFM micrographs and profiles of them for such samples show regular triangle-shaped terraces of 0.95 nm height, which correspond to one quintuple of the layered tetradymite-type structure of Bi$_2$Te$_{3-x}$Se$_x$ films.

The surface (roughness) layer is assumed to be a mixture of 70% diamond and 30% voids and has been described using the Bruggeman effective medium approximation, which can be successfully used to simulate the optical functions of surface roughness and interface layers. We performed the simulations by regression analysis and obtained the spectra of the real and imaginary parts of the dielectric constant for the entire set of MOVPE Bi$_2$Te$_{3-x}$Se$_x$ films (16 samples) under study. To find out the correlation of some parameters, all spectra were fitted several times using different sets of starting parameters. Each time the fitting procedure gave the same result. The results of modeling for five Bi$_2$Te$_{3-x}$Se$_x$ films with different $x$ are shown in figure 3.

The most explicit changes in the spectra of optical parameters of Bi$_2$Te$_{3-x}$Se$_x$ films depend on their composition $x$. The changes of parameters are observed in the red and near-IR spectral regions, while the short-wave part of the spectra is only slightly sensitive to the composition of the films (figure 3).

Figure 3. Spectral dependence of the real $\varepsilon_1$ (a) and imaginary $\varepsilon_2$ (b) parts of the dielectric function for five Bi$_2$Te$_{3-x}$Se$_x$ films with $x$ = 0, 0.25, 0.48, 1.5, 3.0 (curves 1÷5, correspondingly).

Figure 4 shows how the spectral position of the maximum of the imaginary parts ($\varepsilon_2$) of the dielectric function depends on the chemical composition of the Bi$_2$Te$_{3-x}$Se$_x$ films under study. It should be mentioned that this maximum is observed in the long-wave part of the spectra.
In a wide range of concentrations $x$, the position of the maximum monotonously changes with the film composition which makes it possible to use the spectroscopic ellipsometry data to determine the composition of MOVPE Bi$_2$Te$_{3-x}$Se$_x$ films. The value of the real parts ($\varepsilon_1$) of the dielectric function in the 800 - 900 nm range is also suitable for rapid assessment of the composition of Bi$_2$Te$_{3-x}$Se$_x$ films by SE measurements (figure 3, (a)).

Figure 4. The correlation between the position of the maxima in $\varepsilon_2$ spectra of the Bi$_2$Te$_{3-x}$Se$_x$ films under study and their chemical composition. The dashed line connecting the points is just a guide to the eye.

Published data on the Bi$_2$Te$_3$ -Bi$_2$Se$_3$ system are inconsistent. For example, some authors [9] declare that Bi$_2$Te$_{3-x}$Se$_x$ compounds can be considered as a system with limited solid solutions with the Bi$_2$Te$_2$Se compound below the solidus line (500°C). Our XRD and SE data on the monotonous change of the lattice parameters and optical properties of Bi$_2$Te$_{3-x}$Se$_x$ films vs. their composition are in agreement with the concept of the formation of a continuous series of solid solutions due to the progressively full occupation of the internal rows in the five-layered Te-Bi-Se (Te) -Bi-Te blocks by selenium atoms.

4. Conclusion
Rhombohedral Bi$_2$Te$_{3-x}$Se$_x$ films were grown by MOVPE on (0001) Al$_2$O$_3$ substrates. For the first time, the epitaxial Bi$_2$Te$_{3-x}$Se$_x$ films were grown over the entire composition range ($0 \leq x \leq 3$) by the same technique. The good crystal structure and high surface quality of films with a thickness of about 500 nm has been confirmed by X-ray diffraction and atomic force microscopy. It was demonstrated that multi-angle SE is a powerful technique to study optical properties of Bi$_2$Te$_{3-x}$Se$_x$ films. There is no expected inflection at the composition dependence of the optical properties of films under study, especially near the composition $x = 1$, at which selenium atoms fully occupy the internal rows in the five-layered Te-Bi-Se (Te) -Bi-Te blocks. Our work shows the tunability and feasibility of using MOVPE for the preparation of Bi$_2$Te$_{3-x}$Se$_x$ films, offering wide opportunities for exploring topological properties and device applications based on these compositions.

Acknowledgments
The authors are grateful to V.A Luzanov and A.G. Temiryazev for the X-ray and AFM studies of the samples. This work was supported by the Russian Science Foundation, grant N17-19-01057.

References
[1] Hasan M Z and Kane C L 2010. Rev. Modern Phys. 82 3045
[2] Zhang H, Liu C, Qi X, Dai X, Fang Z and Zhang S 2009 Nat. Phys. 5 438
[3] da Silva L W, Kaviany M and Uher C 2005 J. Appl. Phys. 97 114903
[4] Wang Y, Liu S, Yuan J, Wang P, Chen J, Li J, Xiao S, Bao Q, Gao Y and He J 2016 Scientific Reports 6 33070
[5] Smirnov A M, Laktaev I D, Kuznetsov P I and Golant K M 2018 Proc. SPIE 10684 106842K
[6] He L, Kou X and Wang K L 2013 Phys. Status Solidi RRL 7 50
[7] Hirahara T, Sakamoto Y, Takechi Y, Miyazaki H, Kimura S, Matsuda I, Kakizaki A and Hasegawa S 2010 Phys. Rev. B 82 155309
[8] Park D, Park S, Jeong K, Jeong H-S, Song J-Y and Cho M-H 2016 Scientific Reports 6 19132
[9] Sokolov O B, Skipidarov S Y, Duvankov N I and Shabunina G G 2004 J. Cryst. Growth 262 442
[10] Tung Y et al., 2016 J. Appl. Phys. 119 055303
[11] Dubroka A, Caha O, Hroncek M, Fris P, Orilita M, Holy V, Steiner H, Bauer G, Springholz G and Humlicek J 2017 Phys. Rev. B 96 235202
[12] Kuznetsov P I, Yakushcheva G G, Luzanov V A, Temiryazev A G, Shchamkhalova B S, Jitov V A and Sizov V E 2015 J. Cryst. Growth 409 56
[13] Peiguang Y, Rongyong L, Shuangchen R, Aijiang L, Chen H, Zheng Y, Chen S, Guo C and Hu J 2015 Sci. Reports 5 8690
[14] Kuznetsov P I, Savelyev E A, Jitov V A and Golant K M 2018 J. Phys.: Conf. Ser. 1092 012073
[15] Mohamed B, Allel M, Bendouma D, Miloude B and Baghdad M 2018 Mater. Res. 21 20170553
[16] Jariwala B, Shah D and Ravindra N M 2015 Thin Solid Films 589 396
[17] Kovalev V I, Rukovishnikov A I, Kovalev S V and Kovalev V V 2016 J. Opt. Technol. 83 181
[18] Kovalev V I, Rukovishnikov A I, Rossukanyi N M, Kovalev S V, Kovalev V V, Amelichev V V, Kostyuk D V, Vasil’ev D V and Orlov E P 2016 Instrum Exp Tech 59 707
[19] Kovalev V I, Rukovishnikov A I, Kovalev S V, Kovalev V V and Rossukanyi N M 2017 Opt. Spectrosc. 123 168
[20] Kovalev V I, Ali M, Kovalev S V and Kovalev V V 2014 Opt. Spectrosc. 117 118
[21] Kovalev V I, Kuznetsov P I, Zhitov V A, Zakharov L Yu, Rukovishnikov A I, Khomich A V, Yakushcheva G G and Gaponenko S V J. Appl Spectrosc 2002 69 298
[22] Komarov F F, Leontyev A V, Khomich A V and Kovalev V I 2005 Vacuum 78 617