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Crystal growth of Bi_2Te_3 and noble cleaved (0001) surface properties

V.V. Atuchin [a,b,*], V.A. Golyashov [c,d], K.A. Kokh [e,f,g], I.V. Korolkov [d,h], A.S. Kozhukhov [d,i], V.N. Kruchinin [j], I.D. Loshkarev [k], L.D. Pokrovsky [a], I.P. Prosvirin [d,l], K.N. Romanyuk [m,n], O.E. Tereshchenko [c,d,g]

[a] *Laboratory of Optical Materials and Structures, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia*
[b] *Functional Electronics Laboratory, Tomsk State University, Tomsk 634050, Russia*
[c] *Laboratory of Molecular Beam Epitaxy of III-V Semiconductors, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia*
[d] *Novosibirsk State University, Novosibirsk 630090, Russia*
[e] *Laboratory of Crystal Growth, Institute of Geology and Mineralogy, SB RAS, Novosibirsk 630090, Russia*
[f] *Laboratory of Nanostructured Surfaces, Tomsk State University, Tomsk 634050, Russia*
[g] *Spintronics Laboratory, Saint Petersburg State University, Saint Petersburg 198504, Russia*
[h] *Laboratory of Crystal Chemistry, Nikolaev Institute of Inorganic Chemistry, SB RAS, Novosibirsk 630090, Russia*
[i] *Laboratory of Nanodiagnostics and Nanolithography, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia*
[j] *Laboratory for Ellipsometry of Semiconductor Materials and Structures, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia*
[k] *Laboratory of Molecular Beam Epitaxy of Elementary Semiconductors and A3B5 Compounds, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia*
[l] *Boreskov Institute of Catalysis, SB RAS, Novosibirsk 630090, Russia*
[m] *Department of Materials and Ceramic Engineering & CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*
[n] *Institute of Natural Sciences, Ural Federal University, Ekaterinburg 620083, Russia*

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ABSTRACT

A high quality Bi_2Te_3 crystal has been grown by Bridgman method with the use of rotating heat field. The phase purity and bulk structural quality of the crystal have been verified by XRD analysis and rocking curve observation. The atomically smooth $Bi_2Te_3(0001)$ surface with an excellent crystallographic quality is formed by cleavage in the air. The chemical and microstructural properties of the surface have been evaluated with RHEED, AFM, STM, SE and XPS. The $Bi_2Te_3(0001)$ cleaved surface is formed by atomically smooth terraces with the height of the elemental step of $\sim 1.04 \pm 0.1$ nm, as estimated by AFM. There is no surface oxidation process detected over a month keeping in the air at normal conditions, as shown by comparative core level photoelectron spectroscopy.

1. Introduction

Bismuth telluride, Bi_2Te_3, is a representative member of the Bi_2Se_3 crystal family well-known for its pronounced layered crystal structure and good thermoelectric properties [1–5]. Recently, Bi_2Te_3 has become of wide research interest as a three-dimensional topological insulator (TI) where the novel state of quantum matter is realized [6–13]. Such electronic system possesses strong spin-orbit coupling that provides a combination of an insulating bulk and massless Dirac fermion surface states. The experimental realization of TI states was carried out by several methods including thin film and nanoplate preparation [9,10,12,14–16]. Besides this, it is well known that Bi_2Se_3 family crystals possess good cleavage properties and high-quality (0001) surface of macroscopic area can be prepared using the bulk crystal and cleavage procedure [5,7,17–24]. This method of the pristine surface preparation was used in many experiments on TI effect observation and top surface engineering of Bi_2Se_3–family crystals. Regrettably, as a rule, only a very short description of the crystal growth conditions and surface preparation conditions can be found in literature [7,17,18,21–30]. The formation and stability of the TI state at the crystal–vacuum (or air) boundary and device

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[*] Correspondence to: Institute of Semiconductor Physics, 630090 Novosibirsk 90, Russia. Fax: +7 383 3332771.
E-mail address: atuchin@thermo.isp.nsc.ru (V.V. Atuchin).

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structures in particular, however, may be strongly dependent on the structural and chemical qualities of the Bi_2Te_3 crystal and the cleaved surface properties seem to be among governing factors. The present study is aimed at the growth of a high quality Bi_2Te_3 crystal and evaluation of structural and chemical parameters of the cleaved (0001) surface.

Commonly, the surface of telluride compounds is not inert in the air and tends to oxidize due to drastic affinity for oxygen [31–35]. For many complex halcogenide compounds, the chemical interaction with air agents results in a complete decomposition and amorphization that limit the crystal living period. From this point of view, Bi_2Te_3 seems to be not an exception and the presence of oxygen could be expected at the crystal surface. Indeed, oxide presence at the surface of Bi_2Te_3 nanocrystals fabricated by very different techniques was found by XPS in several experiments [36–39]. The behavior of the cleaved Bi_2Te_3(0001) surface is evidently different. The swift oxygen adsorption was detected when the cleaved surface was prepared in the dry nitrogen atmosphere [40]. On the other hand, the Bi_2Te_3(0001) surface cleaved in the air and immediately measured with XPS shows the absence of an oxygen signal [41]. However, the pronounced oxidation was detected even after 4 h keeping in the air atmosphere at $T=24$ °C, and that indicates active chemical interaction of the cleaved Bi_2Te_3(0001) surface with the air agents [41]. It should be pointed that the parallel formation of Bi_2O_3- and TeO_2-type species was found at the surface in this experiment.

Many versions of the Bi–Te equilibrium phase diagram can be found in the literature, and at least one intermetallic phase, Bi_2Te_3, is generally accepted at Bi:Te=1:1 [42–44]. The crystal structure of trigonal Bi_2Te_3, space group R-3 m, $a=4.3896$ and $b=30.5090$ Å, $Z=3$, is shown in Fig. 1 [45,46]. The crystal lattice is formed by the bilayers of face-sharing $BiTe_6$ octahedrons (quintuple). The bilayers are stacked along the c axis by weak van der Waals bonds with as long Te–Te distance as 364 pm. This layered structure provides excellent cleavage properties of Bi_2Te_3 and other members of the Bi_2Se_3 crystal family. On cleavage, the long interlayer Te–Te bonds are disrupted and the (0001) surface is supposed to be Te-terminated. In addition, it should be noted that the phase transition of Bi_2Te_3 into the Bi_2Te_3 II modification, R-3m, $a=4.417$ and $b=29.84$ Å, $Z=3$, was found at a higher temperature and pressure [47]. This orthorhombic modification is metastable under normal conditions. Other properties of the Bi_2Se_3 II phase are unknown.

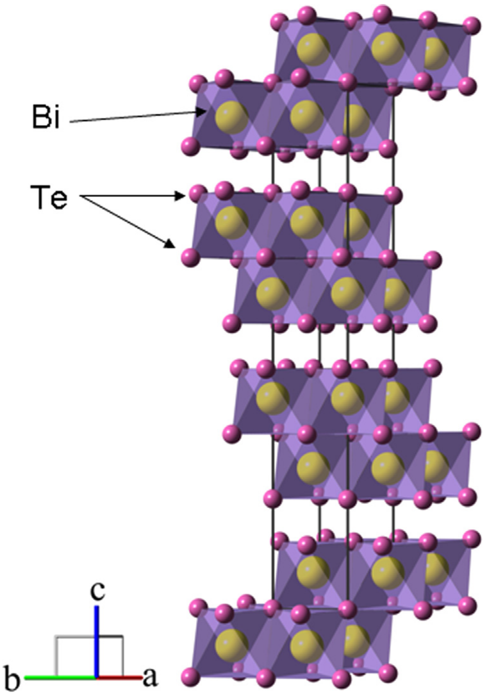

Fig. 1. The crystal structure of Bi_2Te_3. The unit cell is outlined. The lone atoms are omitted for clarity.

2. Experimental

Bi_2Te_3 melts congruently at $T=586$ °C forming eutectic in the Te-rich part of the Bi–Te system [42–44]. The Bi-rich part of the diagram is more complicated consisting of a series of peritectic reactions that is very similar to the behavior of the Bi-Se system [48]. Because of active Bi–Te melt oxidation in the air atmosphere, the crystal growth should be carried out in evacuated quartz ampoules. A vapor pressure of the Bi and Te elementary components at the Bi_2Te_3 melting temperature is far lower than the ampoule resistance threshold (~15 kbar), and the charge may be obtained by direct alloying of the components.

In the present work, the charge prepared from elementary Bi (5 N) and Te (4 N) at stoichiometric composition Bi_2Te_3 was sealed into the quartz ampoule evacuated to $\sim 10^{-4}$ Torr. High-purity bismuth was prepared in NIIC (Novosibirsk, Russia) [49]. The mixture heated up to 20 °C above the melting temperature was left for 1 day for homogenization. Then, after cooling, the synthesized polycrystalline ingot was reloaded to the growth quartz ampoule with a conical tip for recrystallization by the modified vertical Bridgman method with a rotating heat field [50,51]. The ampoule translation rate and axial temperature gradient were 10 mm/day and ~15 °C/cm, correspondingly. The rotating heat field parameters were the same as those earlier used for the $AgGaS_2$ crystal growth [51]. The seed technique was not used. However, the conical ampoule tip resulted in the geometrical selection of the single grain at the initial growth stages. The crystallographic orientation of the grain was (0001) plane nearly along the growth axis that is a common feature of layered chalcogenide crystals [19,52–55].

The phase compositions of both synthesized and recrystallized Bi_2Te_3 were evaluated by X-ray diffraction (XRD) analysis. The XRD patterns were recorded using Shimadzu XRD-7000 (Cu Kα radiation, Ni – filter, 5–60° 2θ range) device. The polycrystalline or single-crystal samples were gently ground with hexane in an agate mortar and the resulting suspension was deposited on the polished side of a standard fused-quartz sample holder, a smooth thin layer being formed after drying. The indexing of the diffraction patterns was carried out using the known structural data [45].

The Bi_2Te_3(0001) substrates with the typical dimensions of $8\times10\times1$ mm^3 were prepared by cleaving the crystal with a steel knife in the air atmosphere. The structural quality of the crystal bulk was estimated by the rocking curve measurements. The X-ray rocking curves were recorded using a two-crystal diffractometer DSO-1T ($Cu_{K\alpha1}$ radiation, $\lambda=1.54056$ Å, Ω–2θ scanning, detector aperture is 170 s of arc) equipped with the Ge(004) monochromator [56]. The top-surface crystallographic properties were evaluated with RHEED using an EFZ4 device under electron energy 50 keV [56–58]. RHEED observation was produced during an hour after crystal cleavage. The surface micromorphology of Bi_2Te_3(0001) substrates was studied by AFM with Solver P-47H device in the noncontact mode [26,59]. The STM images and profile measurements were made at room temperature in an UHV chamber with base pressure $\sim 1\times10^{-10}$ Torr with a Omicron scanning tunneling microscope (STM) on the Bi_2Te_3(0001) samples prepared by cleavage [26,60].

The electronic properties of the Bi_2Te_3(0001) surface were characterized by X-ray photoelectron spectroscopy (XPS). The XPS