Proceedings of the 3rd International Symposium on Scanning Probe Spectroscopy, SPS'03

STM and STS Investigations of Bi_2Te_3 Surface

Sz. Winiarz[a,*], R. Czajka[a,b], S. Suto[c], P. Lośtak[d], S. Szuba[a] and A. Kasuya[b]

[a]Faculty of Technical Physics, Poznan University of Technology
Nieszawska 13A, 60-965 Poznań, Poland
[b]Center for Interdisciplinary Research, Tohoku University
Aramaki-Aza, Aoba-ku, 980-8578 Sendai, Japan
[c]Dept. of Physics, Graduate School of Science, Tohoku University
980-8578 Sendai, Japan
[d]University of Pardubice, Studentska 84, 53210 Pardubice, Czech Republic

We carried out scanning tunneling microscopy/spectroscopy studies of Bi_2Te_3 surface, which, to the best of our knowledge, had not been attempted so far. We got images of surface of the material in many scales from micrometers to nanometers, which showed a layered structure of Bi_2Te_3, with many monoatomic terraces. We found agreement between measured heights and corresponding bulk crystal structure derived from X-ray data. In nanoscale we obtained an atomic resolution. Using scanning tunneling spectroscopy we carried out examination of the electronic structure. We observed different $I-V$ characteristics and contrast on current imaging tunneling spectroscopy maps on non equivalent terraces. The $\mathrm{d}I/\mathrm{d}V$ ($\sim$ density of states) curves referred to those terraces were compared with theoretically calculated by Larson et al. density of states derived from Bi p and Te-1 p orbitals. The analysis of our results allowed us to distinguish bismuth from tellurium planes.

PACS numbers: 68.37.Ef, 61.48.+w

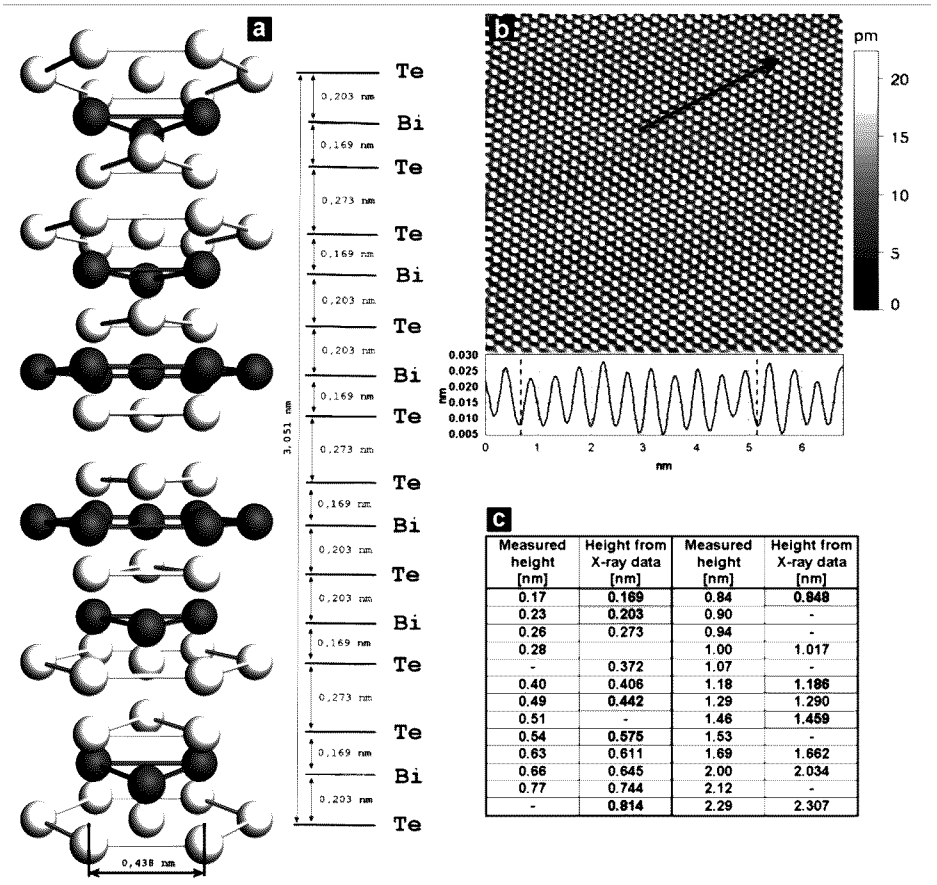
1. Introduction

Many papers about Bi_2Te_3 and related materials concerning such topics as band structure studies through calculations and photoemission experiments have been published in recent years. This compound has also attracted considerable

*corresponding author; e-mail: winiarz@phys.put.poznan.pl

attention because of its potential application in the micro-fabrication of integrated thermoelectric devices [1].

Bi_2Te_3 is a narrow gap semiconductor. The values of an indirect gap obtained through theoretical calculations reported in [2] is 0.11 eV, in [3] is 0.17 eV and in [4] is 0.13 eV. An experimental band gap is 0.15 eV [5]. It is a layered material with a rhombohedral crystal structure of D_{3d}^5 ($R\bar{3}m$) space group. The unit cell contains five atoms [6]. It is also possible to get a hexagonal unit cell as shown in Fig. 1a. Along the z direction, Bi_2Te_3 unit cell consists of five layers bonded by strong ionic and covalent interaction. These so-called "quintuple layer leaves" are connected by weak van der Waals type bonds [4]. Atom layers occur in the sequence: Te(1)–Bi–Te(2)–Bi–Te(1), where the Te(1) and Te(2) are nonequivalent tellurium sites [5].



c

Measured height [nm]	Height from X-ray data [nm]	Measured height [nm]	Height from X-ray data [nm]
0.17	0.169	0.84	0.848
0.23	0.203	0.90	-
0.26	0.273	0.94	-
0.28		1.00	1.017
-	0.372	1.07	-
0.40	0.406	1.18	1.186
0.49	0.442	1.29	1.290
0.51	-	1.46	1.459
0.54	0.575	1.53	-
0.63	0.611	1.69	1.662
0.66	0.645	2.00	2.034
0.77	0.744	2.12	-
-	0.814	2.29	2.307

Fig. 1. Hexagonal unit cell (a), atomic resolution STM image (b), measured heights of the steps (c) (e.g. as seen in Fig. 2e).

In this paper we present the results of Bi_2Te_3 studies using scanning tunneling microscopy/spectroscopy (STM/STS) techniques, which, to the best of our knowledge, have not been attempted before. We recorded images of the material's surface in many scales (from micrometers to nanometers), which show a layered structure of Bi_2Te_3, with many monoatomic terraces. We have compared our measured heights with heights which can be calculated using the X-ray data [6]. We also performed current imaging tunneling spectroscopy (CITS) measurements and local density of states was calculated using Bando et al. method [7].

2. Experimental details

Bismuth and tellurium of 5N purity were used for preparation of the Bi_2Te_3 crystal. The compound was first synthesized from the elements in conical ampoules of 10 mm in diameter. After being evacuated and sealed off, the ampoule was annealed at a constant temperature of 1276 K for 48 h. Then the ampoule was lowered at rate of 4.5 mm/h into a region of temperature gradient of 400 K/5 cm. Single crystals of 10 mm in diameter and about 50 mm length were obtained. In almost all cases the c axis was perpendicular to the growth direction, i.e., the (0001) plane was perpendicular to the axis of conical ampoule. The middle parts of a single crystal were used for the investigation [8].

The original sample was cut into small ($5 \times 5 \times 4$ mm) pieces. One side of that box-shaped sample is a plane parallel to atomic layers. The crystal was cleaved using adhesive tape. That procedure, in most of the cases, gave us a sample with clean, flat and contamination free surface. This preparation procedure is simple and effective, because layer–layer interaction have a weak van der Waals origin whereas bonding within layers is ionic or covalent [6]. The sample prepared in such a way was then transferred to an UHV (10^{-9} Torr) chamber equipped with an Omicron STM/AFM microscope. All measurements presented here were done in ambient temperatures.

3. Experimental results and discussion

Pictures taken at large magnification revealed a hexagonal order of atoms in particular layers. A lattice constant measured as shown in Fig. 1b is 0.45 ± 0.01 nm. This value is very close to the literature data — 0.438 nm [6].

Figure 1c shows statistically most frequent heights observed during our measurements (e.g. as seen in Fig. 2e). The right hand column represents possible distances between observed layers which would be created on the surface assuming that it is a random process. The table cells marked with darkened background show the distances in nanometers between layers of different atoms. Some of the distances, e.g. 0.372 nm corresponding to Bi–Te(1) bilayer, were not observed.

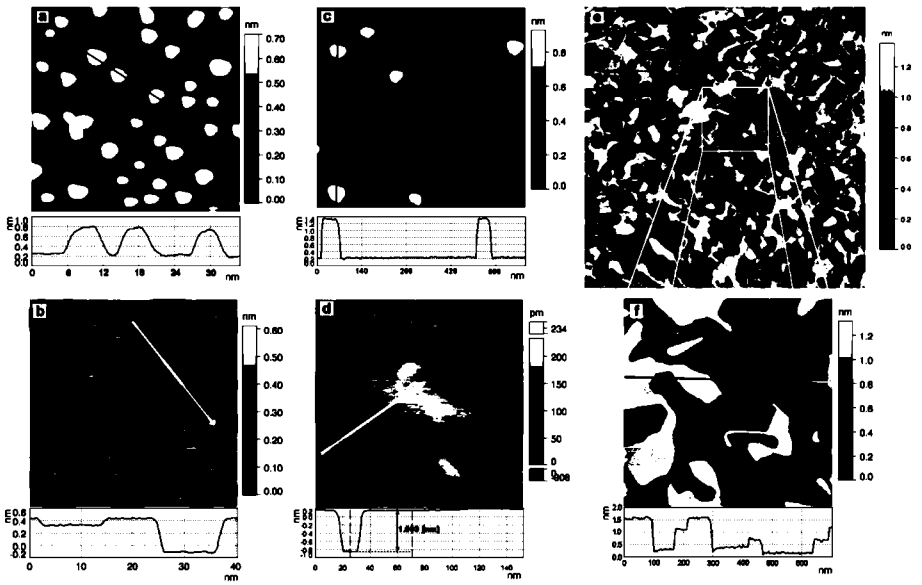


Fig. 2. Surface of Bi_2Te_3 (a) and (b) after cleavage, area of 64×64 nm^2, (a) islands $h = 0.49 \pm 0.1$ nm, size 6–12 nm, (b) case with holes, depth 0.51 ± 0.02 nm, size ~ 7 nm. After heating at 150–200°C: (c) 700×700 nm^2, islands' $h = 1.13 \pm 0.03$ nm, size 50–60 nm; (d) 256×256 nm^2, holes' size ~ 20 nm, depth ~ 1 nm. Surface after elongated annealing at 130°C: (e) 2500×2500 nm^2, (f) magnification of a part of (e).

Figure 2a shows the surface of the Bi_2Te_3 sample directly after being cleaved and transferred into UHV. It appears as an atomically flat plane with little triangular islands. Islands' height was 0.49 ± 0.1 nm, and their dimensions were approximately 6–12 nm. Probably they are formed with atoms that were torn out from the removed layers during cleaning process mentioned above. Energy in the room temperature is not sufficient for the triangular forms to migrate. In some cases the cleaning process gave us a different surface morphology. In principle it looked the same, but then we observed triangular holes in atomically flat areas. Theirs depth was 0.51 ± 0.02 nm, and dimensions were about 7 nm in each direction (Fig. 2b). The X-ray data analysis allowed us to conclude that the basic planes consisted of tellurium atoms and the Bi planes were placed below and above the Te one.

Heating the sample changed the structure of surface. We used two different temperatures and durations. At first it was 150–200°C with duration of 1–3 h and the process was accomplished with annealing at 120°C with times longer than 48 h.

Due to a higher temperature and longer period of time that had been passed since cleavage, the surface exhibited a little bit different structure. The small and dense-packed triangular pieces migrated and formed much larger almost hexagonal shape islands (Fig. 2c). Islands dimensions are about 50–60 nm, and the

height of all islands on average was 1.13 ± 0.03 nm. According to X-ray data the nearest possible sequences of atomic layers which may create such an island are: substrate(Bi)–Te(1)–Te(1)–Bi–Te(2)–Bi–Te(1) and substrate(Te(1))–Bi–Te(2)–Bi–Te(1)–Te(1)–Bi. Both have identical height — 1.186 nm. Therefore we can assume that the upper most atoms of island and substrate are of different kind in any case. Adequately, if a cleaved surface was of a second kind (holes instead of islands) we observed the creation of larger triangular holes as a result of the annealing process (Fig. 2d). The measured depth was 1.003 ± 0.032 nm. This value agrees with 1.017 nm calculated from the X-ray data [6]. It is the thickness of every six subsequent atomic layers, so it follows that they are of the same kind. If we take into account that the Bi_2Te_3 crystal should cleave along the Te(1)–Te(1) bonds, (because they are of van der Waals type) we can conclude that atomic layers sequence from most top layer to the bottom one is: Te(1)–Bi–Te(2)–Bi–Te(1)–bottom(Te(1)).

The surface evolved to a quite complex structure as a result of prolonged (> 48 h) annealing time at 120°C. Figure 2e shows an example picture of that surface with many terraces, placed on different heights. Most of the topographic formations do not have a clear hexagonal symmetry as mentioned earlier islands/holes had. Those miscellaneous terraces exhibit different shapes and heights. Assuming that terraces maintain the atomic structure of Bi_2Te_3, a distance between any pair

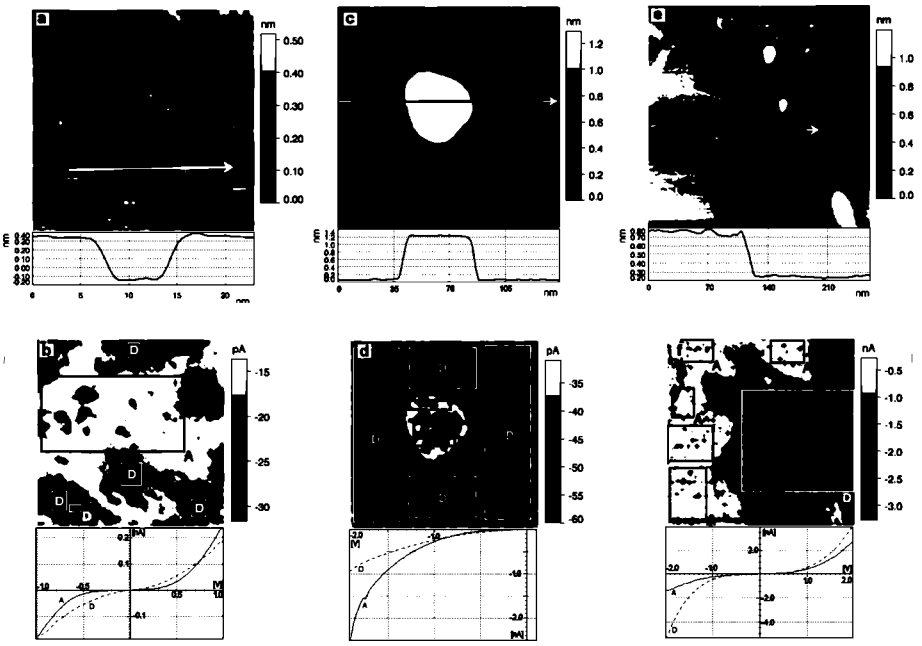


Fig. 3. Topography images (top row) and corresponding CITS maps (bottom row).

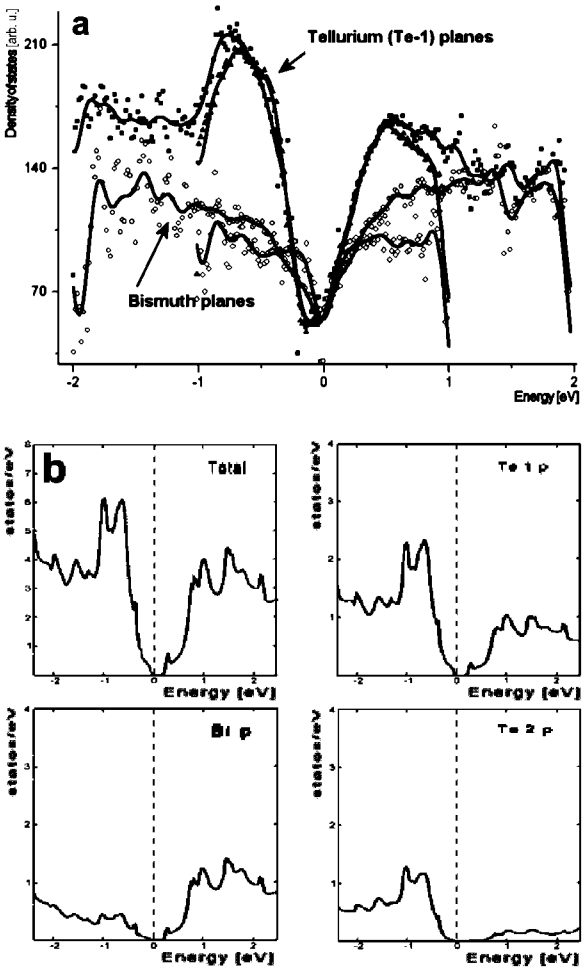


Fig. 4. (a) Calculated LDOS curves vs. energy for bismuth and tellurium terraces in Bi_2Te_3; (b) DOS vs. energy theoretically calculated by Larson et al. [4] (with the authors' permission).

of the visible layers should agree with the adequate pair of planes from the X-ray data. We observed the consistence between our STM measurements and X-ray data in most cases as it is seen in Fig. 1c.

CITS maps revealed areas with different electronic properties. In particular, there was no contrast when terraces were spaced (in z direction) by the distance among equivalent atomic layers. For example when the height was 0.49 nm (Fig. 3a), which corresponds tellurium and bismuth planes, we could see a clear contrast on the CITS image. Contrary, there was no contrast when observing the same atomic planes as in Fig. 3f (indicated by arrows). The difference in height

was about 0.61 nm which is close to the space between Bi planes. The step height between largest terraces was 0.58 ± 0.01 nm and there is a clear contrast in the CITS map as we expected.

We also calculated curves of the local density of states (LDOS) at different terraces using Bando et al. [7] method. They are presented in Fig. 4a. Comparing these the curves with theoretically calculated DOS vs. energy [2, 4] (Fig. 4b) we can conclude that the curve measured above the top terrace (left side in Fig. 3f) is similar to DOS of Bi p orbital presented in [4]. Adequately the curve measured above the bottom terrace resembles the DOS curve of Te-1 p orbital [4].

4. Conclusions

Our STM investigations of the Bi_2Te_3 surface revealed the presence of the atomically flat terraces with small triangular shaped islands or holes. The prolonged annealing developed the multi-terraces surface structure. The steps' heights were correlated with the X-ray data. CITS maps exhibited the contrast between terraces representing different atomic planes. The $\mathrm{d}I/\mathrm{d}V$ ($\sim$DOS) curves referred to those planes were compared with theoretically calculated DOS and allowed us a distinction between bismuth and tellurium planes.

Acknowledgments

As regards Polish authors, this work was done under PB 62-198/03-BW.

References

[1] Gao Min, D.M. Rowe, *Solid-State Electron.* **43,** 923 (1999).

[2] S.K. Mishra, S. Satpathy, O. Jepsen, *J. Phys., Condens. Matter* **9,** 461 (1997).

[3] P. Larson, V.A. Greanya, W.C. Tonjes, Rong Liu, S.D. Mahanti, *Phys. Rev. B* **65,** 085108 (2002).

[4] P. Larson, S.D. Mahanti, *Phys. Rev. B* **61,** 8162 (2000).

[5] G.A. Thomas, D.H. Rapkine, R.B. Van Dover, L.F. Mattheis, W.A. Surden, L.F. Schneemaper, J.V. Waszczak, *Phys. Rev. B* **46,** 1553 (1992).

[6] R.W.G. Wyckoff, *Crystal Structures*, Vol. 2, Krieger, London 1986 and references therein.

[7] H. Bando, T. Shimitzu, Y. Aiura, Y. Haruyama, K. Oka, Y. Nishihara, *J. Vac. Sci. Technol. B* **14,** 1060 (1996).

[8] R. Czajka, J. Horak, P. Lostak, S. Karamazov, J. Vanis, J. Walachova, *J. Vac. Sci. Technol. B* **18,** 1194 (2000).