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Authors: A.I. Komonov, V.Ya. Prinz, V.A. Seleznev, K.A. Kokh, V.N. Shlegel



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Step-height standards based on the rapid formation of monolayer steps on the surface of layered crystals

A I Komonov¹, V Ya Prinz¹, V A Seleznev¹, K A Kokh², V N Shlegel³

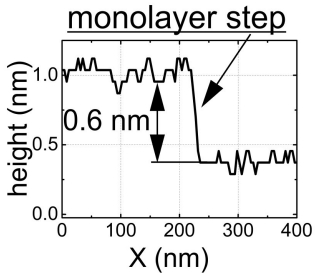
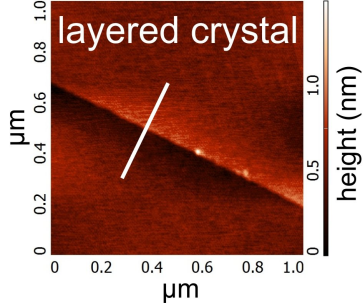
1 Rzhanov Institute of Semiconductor Physics, Siberian Branch of the Russian Academy of Sciences (ISP SBRAS), pr. Lavrentieva 13, Novosibirsk, Russia, 630090;

2 Sobolev Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences (IGM SB RAS), pr. Koptyuga 3, Novosibirsk, Russia, 630090;

3 Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences (NIIC SB RAS), pr. Lavrentieva 3, Novosibirsk, Russia, 630090;

E-mail: prinz@isp.nsc.ru

Graphical abstract



Highlights

1. Easily reproducible step-height standard for SPM calibrations was proposed.
2. Step-height standard is monolayer steps on the surface of layered single crystal.
3. Long-term change in surface morphology of Bi_2Se_3 and ZnWO_4 was investigated.
4. Conducting surface of Bi_2Se_3 crystals appropriate for calibrating STM
5. Ability of robust SPM calibrations under ambient conditions were demonstrated.

Abstract

Metrology is essential for nanotechnology, especially for structures and devices with feature sizes going down to nm. Scanning probe microscopes (SPMs) permits measurement of nanometer- and subnanometer-scale objects. Accuracy of size measurements performed using SPMs is largely defined by the accuracy of used calibration measures. In the present publication, we demonstrate that height standards of monolayer step (~ 1 and ~ 0.6 nm) can be easily prepared by cleaving Bi_2Se_3 and ZnWO_4 layered single crystals. It was shown that the conducting surface of Bi_2Se_3 crystals offers height standard appropriate for calibrating STMs and for testing conductive SPM probes. Our AFM study of the morphology of freshly cleaved (0001) Bi_2Se_3 surfaces proved that such surfaces remained atomically smooth during a period of at least half a year. The (010) surfaces of ZnWO_4 crystals remained atomically smooth during one day, but already two days later an additional nanorelief of amplitude ~ 0.3 nm appeared on those surfaces. This relief, however, did not further grow in height, and it did not hamper the calibration. Simplicity and the possibility of rapid fabrication of the step-height standards, as well as their high stability, make these standards available for a great, permanently growing number of users involved in 3D printing activities.

Keywords: calibrating measure, monolayer steps, layered crystals, scanning probe microscopy (SPM), atomic force microscopy (AFM), scanning tunneling microscopy (STM), Bi_2Se_3 and ZnWO_4

1. Introduction

A modern tendency in electronics, photonics and solid-state physics is the reduction of geometric sizes of device features down to few nanometers [1, 2]. Numerous studies were devoted to the handling of individual atoms and their groups as well as small clusters such as quantum dots and other low-dimensional objects possessing fundamentally new functional properties [3]. For manufacturing structures and devices based on nanoobjects, one should be able to create objects with precise geometric sizes decreased down to 1 or even 0.1 nm, since such sizes define characteristics of the final devices. That is why metrology is acutely required for nanomanufacturing, where it assumes a special significance on decreasing the sizes of manufactured objects below 10 nm. In recent years, a new field has emerged in which metrology had become extremely needed for many users; this field is the additive (3D printing) technology [4]. Indeed, the sizes of 3D-printed objects still keep decreasing. By now, metal and polymer nanowires with sizes smaller than 10 nm [5-7] have been demonstrated and nanometer precision has been achieved [8, 9]. The amount of 3D printers in the world permanently grows and, hence, readily available standard measures for them are required.

In the nanometer measuring range, scanning probe microscopy (SPM) has proven to offer a good measuring tool. For instance, a successful use of SPM for controlling characteristics of micro- and nanogrids on 3D-printed curved surfaces was demonstrated in [10, 11]. However, Yu.A. Novikov et al. [12] have showed that, in measurements of one and the same reference stepped structure on scanning probe microscopes purchased from different manufacturers, measured signal traces were different, and they also differed substantially from the shape of real measured objects. The problem of obtaining adequate SPM data has been known for a long time [13] and still is important [14]. The solution to this problem is based on the ability to identify the useful signal [15] and on the ability to single out and examine the geometric properties of surface topography [16]. For adequate measurement of surface topography, calibrations to be made with the help of high-precision standard measures with known geometric sizes are required [17, 18].

Three main types of calibration measures (CMs) for SPM are presently available:

- 1) artificial three-dimensional (3D) structures fabricated by reactive ion etching of silicon surface through an electron-beam resist mask [19, 20];

- 2) atomic steps formed on the surfaces of Si, Al₂O₃ and SiC single crystals [21-24];
- 3) atomic steps on the surface of graphite and mica polycrystals formed by cleaving sample surfaces [25, 26].

Unfortunately, those measures are by no means universal ones, and they possess a number of substantial drawbacks that seriously hamper the calibration procedure. Those drawbacks force the researchers to use several calibration measures for calibrating a single SPM probe, and this makes the calibration procedure too labor-consuming. Typical problems are as follows:

1. The surfaces of CMs of the first and second type show a substantial degradation in time, and they cannot be renovated under ordinary laboratory conditions without using special equipment.
2. As a rule, CMs of the first and second type have a non-conducting working surface; the latter fact makes the calibration of devices and probes using the “current mode” impossible.
3. CMs of the third type are of polycrystalline nature, and they contain a high concentration of various defects (screw dislocation, point defects, grain boundary, dislocation networks, dislocation ranks). As a result, the cleaved CM surface presents 3D structure with complicated topography; this circumstance makes identification of monoatomic steps on such surfaces and calibration on such samples highly problematic [27, 28].
4. CMs of the second and third type have step heights from several angstroms to 1 nm; such measures are inappropriate for calibrating measurements in the range over ten nanometers. CMs of the first type have step heights over ten nanometers, and they cannot be used for calibrations in the range below ten nanometers.

Thus, the measures are not universal, and, for using all available techniques, a number of CMs are required for calibration of SPM in the whole working range of measurements. It is worth noting that, although Si and SiC specimens are used in high-vacuum STM measurements [29, 30] and there exist stepped structures based on such specimens which are used for measuring height in AFM [21-24], nonetheless, under ambient conditions (normal atmospheric humidity and temperature) the surface of such specimens gets covered by natural oxide and degrades rapidly [31, 32]; both circumstances make such calibration measures inappropriate for calibrating devices and probes using “current mode”. The purpose of the present study was the development of a convenient express procedure for calibrating SPM in the ranges of few nanometers, where the above drawbacks are lacking.

Well known that atomically plane single-crystal surfaces with single monolayer step over areas of a few micrometres could be ideal samples for SPM calibration due to low roughness and lack of defects in selected area [17]. A simple convenient procedure for forming such steps by cleaving allows one to avoid the majority of calibration problems that arise when standard calibration measures are used. Cleaving is a good method to obtain a surface which was frequently used for studying the properties of freshly cleaved highly oriented pyrolytic graphite (HOPG) [33] and, in particular, for calibrating various SPM. A step of monolayer height obtained by cleaving is a fundamental quantity, and it can be used as a step-height standard.

In the present paper, we show that a molecular monolayer step on the surface of a high quality layered single crystal with weakly bonded crystal layers can be used as a step-height standard easily reproducible under laboratory conditions. A clean surface with test steps can be obtained prior to measurements, thus cutting both the calibration time and the time required to be consumed for the measurement procedure. In the present study, the possibility of creating a step-height standard has been demonstrated by the example of layered crystals of ZnWO₄ and Bi₂Se₃ with molecular-layer thicknesses of 0.6 and 1 nm.

2. Experimental details

We examined ZnWO_4 single crystals grown from stoichiometric melt using the low thermal gradient Czochralski technique. A distinctive feature of the method is an extremely small temperature gradient in the melt, 0.1-1.0 K/cm, in comparison with the traditional Czochralski growth of which temperature gradients 10-100 K/cm are typical [34].

Also, Bi_2Se_3 single crystals grown by the modified Bridgman-Stockbarger method [35, 36] from 99.99%- pure Bi and Se [37] were examined. The extremely pure bismuth was obtained from the Institute of Inorganic Chemistry [38]. Details of the method were described in [39].

The dimensions of the obtained ingots were 45 mm in diameter and up to 150 mm in length for ZnWO_4 and 9 mm in diameter and up to 60 mm in length for Bi_2Se_3 . With the help of a diamond saw, single crystals sized $10 \times 10 \times 5 \text{ mm}^3$ were cut out from the grown ingots. From the obtained specimens, plates 0.5 to 2 mm thick were cleaved with a steel razor blade in directions parallel to cleavage planes, namely, in the (010) planes for ZnWO_4 and in the (0001) planes for Bi_2Se_3 (see figure 1). Before cleaving samples were washed in boiling toluene for 15 minutes and were washed in isopropyl alcohol under ultrasonic agitation during 15 min. Then, the samples were dried by blowing them with dry clean air. The cleaving procedure was performed manually in antistatic gloves on a clean plastic table surface with the help of clean tweezers and a razor blade. The sample was put with one of its faces onto the table so that the cleavage planes were normal to its upper face. A razor blade oriented along the cleavage planes was brought close to this face while sample was kept fixed with the tweezers. A small force applied to the blade caused the formation of a crack and cleavage of the sample. As a result of the procedure, two samples with clean surfaces were obtained. Those surfaces were free of contaminations and required no subsequent treatments. For Bi_2Se_3 , the cleaving of surface layers was also performed using an adhesive tape.

Right after the cleaving procedure, the sample was mounted in the AFM holder and, following 5 minutes after the cleaving procedure, AFM measurements were performed. During the first day, the measurements were repeatedly performed each 20 min. During the first month after the cleaving procedure, the measurements were performed once a day. Then, over the year, the measurements were repeated once a month. After the cleaving procedure, the sample was stored in a clean plastic Petri dish under room ambient conditions. During the year, the temperature in the room varied in the interval from $+18^\circ\text{C}$ to $+27^\circ\text{C}$, and the relative humidity, in the interval from 20% to 70%.

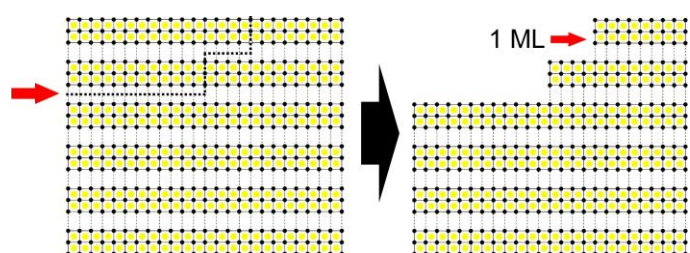


Figure 1. Schematic representation of a layered crystal with steps of monolayer height present on its cleaved surface. The red arrow shows the cleavage direction. The dashed lines indicate the weak bonds between the molecular layers whose rupture gives rise to steps of monolayer height formed on the surface of the material.

The surfaces of the crystals under study were examined on an optical microscope and on an atomic-force microscope. Optical images were obtained on an Altami MET 5 metallographic microscope whose resolution was $1 \mu\text{m}$. A Solver PRO SPM from NT-MDT (Russia) was used to examine the surface morphology of the samples. AFM measurements were carried out in semi-contact mode using standard NSG-11 (NT-MDT) and HA-HR (NT-MDT) cantilevers under ambient conditions. The working ranges of resonance frequency and force constant of NSG-

11 cantilevers were from 115 to 325 kHz and from 2.5 to 22.5 N/m, respectively. The working ranges of resonance frequency and force constant of HA-HR cantilevers were from 350 to 410 kHz and from 27 to 41 N/m, respectively. STM measurements were carried out in direct current mode using as the tip a mechanically cut Pt/Ir wire of 200- μ m diameter. The obtained AFM data were analyzed using the standard NOVA software obtained from NT-MDT (Russia) and more advanced open-source SPM software (Gwyddion) [40].

3. Results and discussion

In our experiments, we examined cleavage of the various layered single crystals with the use of the SPM. It was found that, as a result of cleavage, a fresh surface made up of atomically smooth terraces was formed. The terraces were spaced apart by a distance being multiples of the molecular-layer height of the crystal whose particular values were defined by the type of the layered crystal and presented fundamental quantities. The results of studies of one of the cleaved (0001) Bi_2Se_3 surfaces are presented in Fig.2. Figure 2c shows an AFM image of three molecular-layer height steps with the extracted height spectrum (Fig. 2d). The height of the monolayer steps corresponds to the separations between the peaks of the height distribution function; for (0001) Bi_2Se_3 , this height was found to equal 1.0 ± 0.06 nm. Similar data for a cleaved (010) surface of ZnWO_4 are shown in Fig. 3. The statistical analysis has shown that the height of a monolayer step measured by AFM on the surface of (010) ZnWO_4 was 0.57 ± 0.04 nm (see Figs. 3c and 3d). Our measured data for the height of molecular-layer steps are in agreement with the values that were previously reported in [41-44] (0.955 ± 0.001 nm for Bi_2Se_3 and 0.571 ± 0.001 nm for ZnWO_4).

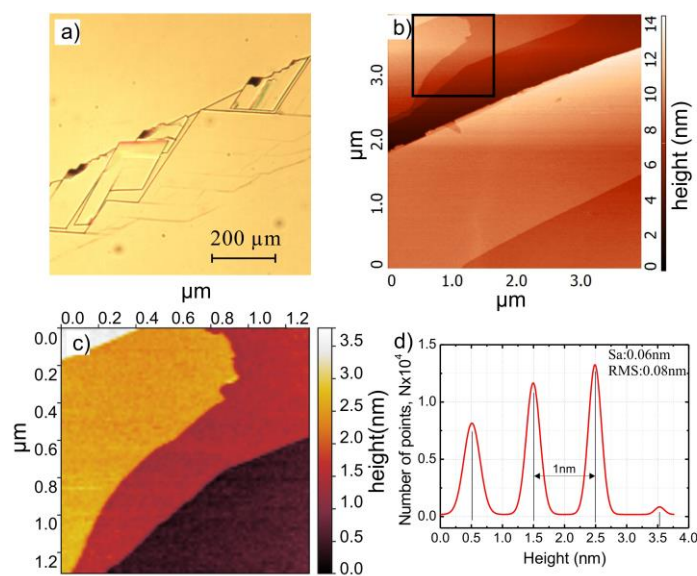


Figure 2. (a) Optical image of a cleaved (0001) Bi_2Se_3 surface. (b) AFM image of a cleaved (0001) Bi_2Se_3 surface. (c) AFM image of a (0001) Bi_2Se_3 surface framed in Fig. 2b. (d) Statistical distribution of height values for Fig. 2c, the height of a monolayer steps corresponds to the separations between the peaks of the distribution function.

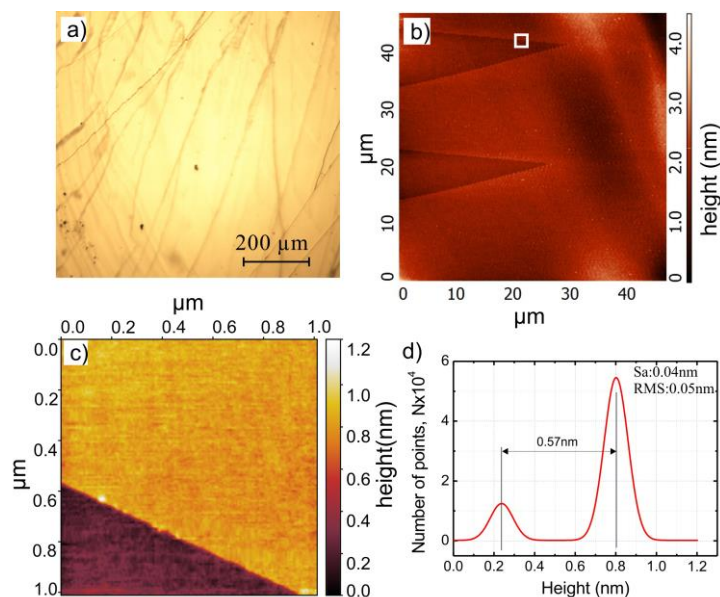


Figure 3. (a) Optical image of a cleaved (010) ZnWO_4 surface. (b) AFM image of a cleaved (010) ZnWO_4 surface. (c) AFM image of a (010) ZnWO_4 surface framed in Fig. 3b. (d) Statistical distribution of height values for Fig. 3c, the height of a monolayer step corresponds to the separation between the peaks of the distribution function.

The above data show that the cleaved surfaces can be used as step-high standard in calibration of AFM facilities; for such applications, it is important to know how stable the surfaces and the steps are under normal environmental conditions. Within the scope of the present study, the problem of surface stability under ambient conditions was specially addressed. In the world literature, there is no consensus of opinion on the phenomenon of surface degradation in chalcogenides. The majority of research teams believe that the surface of chalcogenides crystals undergoes rapid oxidation when stored in air [45-47]. In [48], Green *et al.* reported that “within two hours of exfoliation, a series of $\sim 3.2\text{-\AA}$ high islands were observed by atomic force microscopy over approximately 10% of the (0001) surface of Bi_2Se_3 .” On the contrary, other authors (see [37, 49]) argued that the crystal surface obtained by those authors showed no degradation during a month; moreover, no oxide film formed on this surface at all. In [50], Golyashov *et al.* have shown, using x-ray photoelectron spectroscopy, that the (0001) surface of Bi_2Se_3 proved to be very stable not only to oxidation in O_2 but, also, to oxidation in NO_2 . Moreover, it was found that the crystal surface started undergoing oxidation, for instance, on introduction of an additional amount of defects into samples while treating them in argon plasma. The authors express an opinion that this regularity resulted from the structural perfection of their crystals and from the absence of Se vacancies on the (0001) surface of Bi_2Se_3 , which act to precondition bismuth for subsequent reaction with the oxidant; the latter conclusion was also supported by density functional calculations. In our opinion, the controversy between the results obtained by different research teams can be attributed to the difference between the qualities of examined crystals. In the present study, we have performed an independent examination of Bi_2Se_3 crystals similar to those examined by Atuchin *et al* [37]. An image of a freshly cleaved (0001) surface of Bi_2Se_3 and an image of a sample that has been stored under ambient conditions during a period of six months is shown in figure 4. Indeed, the surface has not demonstrated a visible degradation. As mentioned above, the quality of examined Bi_2Se_3 crystals was perfect. In the case of terraced surfaces with steps, we have identified no time variations of surface morphology under ambient conditions.

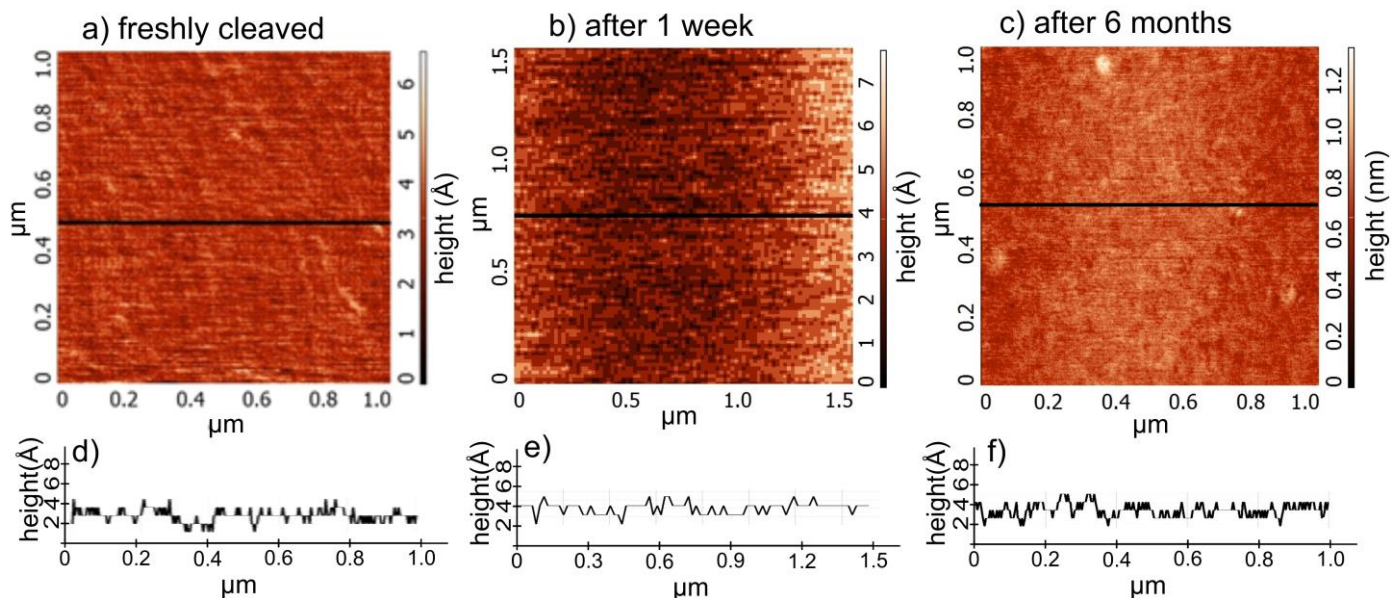


Figure 4. Demonstration of a (0001) Bi₂Se₃ surface stability in time under ambient conditions. (a) AFM image of a freshly cleaved (0001) Bi₂Se₃ surface obtained by cleaving a crystal of Bi₂Se₃ with a sharp steel razor blade along a cleavage plane. (b) AFM image of a (0001) Bi₂Se₃ surface that was exposed to air during a week. (c) AFM image of a (0001) Bi₂Se₃ surface that was exposed to air during a period over 6 months. (d) – (f) Cross-sectional profiles measured on the surface of Bi₂Se₃ along the lines indicated in Fig. 4a. – Fig 4c.

Unlike in the case of (0001) Bi₂Se₃, we have identified a variation in time of the morphology of freshly cleaved (010) surfaces of ZnWO₄ under ambient conditions. As it is known from literature (see, e.g. [44]), a cleaved (010) surface of ZnWO₄ crystals has atomically smooth surface partially made up by chemically active zinc atoms. That is why it can be expected that the cleaved (010) surface of ZnWO₄ will be a surface much more chemically active in comparison with the surface of Bi₂Se₃. This hypothesis was proved via making a comparison between the surface morphology of a freshly cleaved (010) surface of a ZnWO₄ sample and the same surface after the 2-day storage of the sample under ambient conditions (at temperature 25°C and relative humidity 23%). As it is evident from Fig. 5a, c, the freshly cleaved surface is an atomically smooth one, with the surface roughness 0.05 nm RMS. The (010) surface of ZnWO₄ crystals remained atomically smooth during one day, but already two days later an additional nanorelief of amplitude ~0.3 nm appeared with increasing surface roughness to 0.10 nm RMS (see Fig. 5b, d). It seems that the variation of the surface roughness was due to the adsorption of various contaminations and water vapor molecules by the surface from ambient conditions. Foreign molecules adhere to the surface to become bound to chemically active zinc atoms, which likely act as acceptors of contaminating impurities. Note that nanorelief did not further grow in height, but it can hamper the calibration when a terraced surface with steps is used.

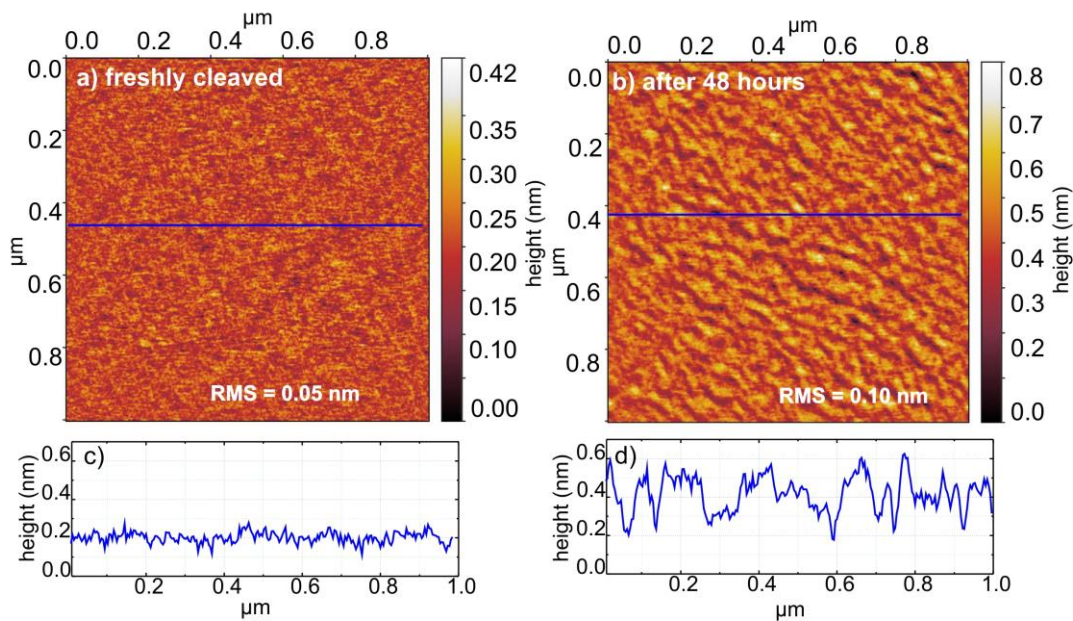


Figure 5. Degradation of a (010) ZnWO₄ surface in time under ambient conditions. (a) AFM image of a freshly cleaved (010) ZnWO₄ surface. (b) AFM image of a (010) ZnWO₄ surface that was exposed to air during a 2 days. (c) – (d) Cross-sectional profiles measured on the surface of ZnWO₄ along the lines indicated in Fig. 5a. – Fig 5b.

Indeed, an increase of surface roughness leads to a greater measurement uncertainty of step height; this regularity is confirmed by the data of Fig.6. For freshly cleaved surface, values $S_a = 0.04$ nm and $RMS = 0.05$ nm were found, whereas after two days values $S_a = 0.09$ nm and $RMS = 0.11$ nm were obtained. The measurement uncertainty of step height and the broadening of distribution-function peaks had increased two-fold, but it did not strongly hamper the calibration.

Note that in the formation of fresh surfaces by cleaving takes about 5 minutes, and the cleaved surface remains atomically smooth during one day. The crystal cleaving process can be repeated many times due to the fact that the thickness of the layer being detached normally amounts to several tens of micrometers parts, and the calibration measure has a thickness of three to five millimeters. Thus we recommend doing the SPM calibration procedure always on freshly cleaved surface of the ZnWO₄ crystals.

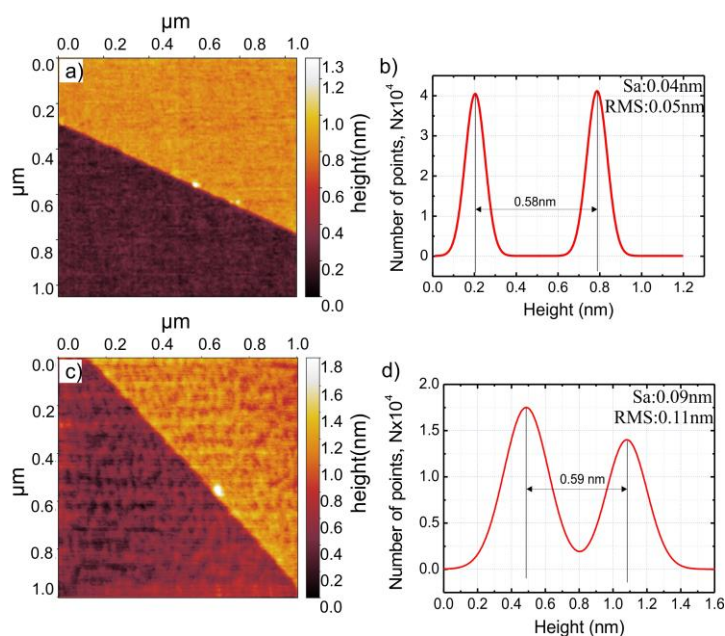


Figure 6. Influence of the surface degradation on the accuracy of measurements of monolayer step. (a) AFM image of a freshly cleaved (010) ZnWO₄ surface. (c) AFM image of a (010) ZnWO₄ surface that was exposed to air during two days. (b), (d) Statistical distributions of height values for Fig. 6a - Fig. 6c.

Also, it was found for Bi₂Se₃ crystals that there existed an interrelation between the cleaving method and the degree of smoothness of the formed surface. If a crystal was cleaved with a sharp steel razor blade parallel to cleavage (0001) planes, then the formed cut contained a minimum amount of atomic steps, and atomically flat surfaces with relatively large sizes ($\sim 0.01 \text{ mm}^2$) and roughness less than 0.06 nm RMS have been prepared (figure 7a - c). Alternatively, if adhesive tape was used to cleave the crystal, then the number of the steps increased sharply, and this number depended on the detachment direction of adhesive tape in the (0001) crystallographic plane (figure 7d - f). Most probably, such a result was due to shear deformations generated by the adhesive tape being detached from the crystal during its non-uniform action on the crystal surface. The attempt to cleave ZnWO₄ crystals with the help of adhesive tape proved to be inefficient. In the latter case, cleavages are to be made with the help of blades. Indeed, the molecular layers of Bi₂Se₃ are bonded together by weak Van-der-Waals forces [51], whereas in ZnWO₄ crystals all bonds are covalent [52], and they differ in their ionicity. The bond strength in covalent ZnWO₄ crystals is one order of magnitude greater in comparison with Bi₂Se₃ Van-der-Waals crystals.

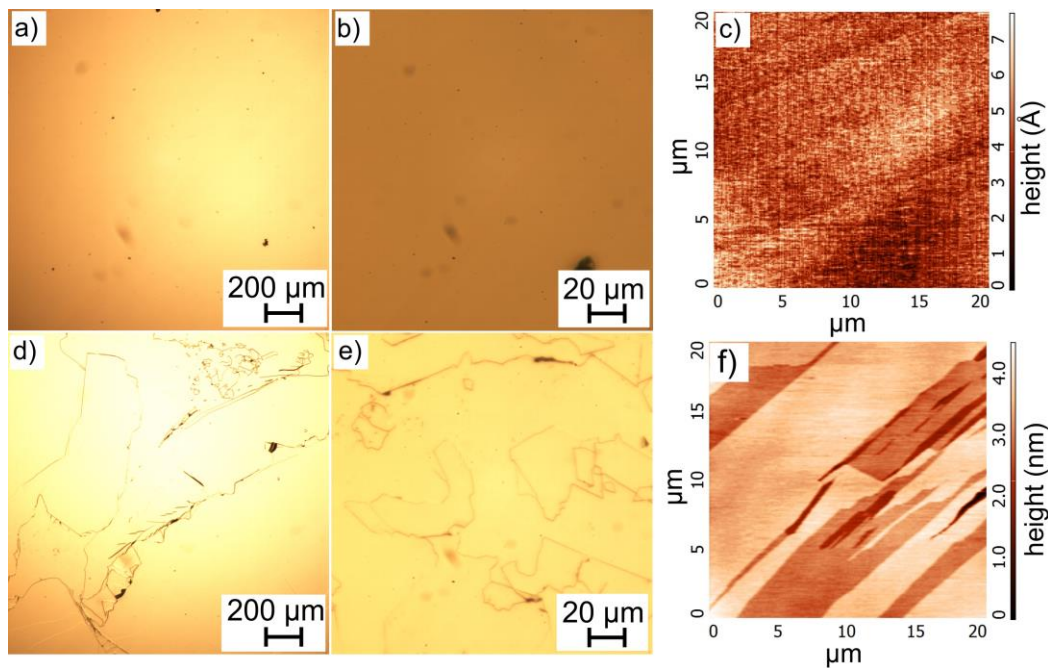


Figure 7. (a, b) Optical image of a (0001) Bi_2Se_3 surface formed by splitting a crystal of Bi_2Se_3 with a sharp steel razor blade along a cleavage plane. (c) Typical AFM image of the surface shown in Fig. 7b. (d, e) Optical image of a (0001) Bi_2Se_3 surface obtained by exfoliating a thin layer of the material with adhesive tape. (f) Typical AFM image of the surface shown in Fig. 7e.

Comparing the properties of the crystals of the two types, we draw attention to the fact that Bi_2Se_3 is a topological insulator with conductive surface [53]. That is why, in addition to AFM measurements, STM and current-voltage measurements (we applied a voltage between the probe in contact mode and our measure) were performed on the surface of Bi_2Se_3 crystals. Those measurements have showed (see figure 8) that (0001) Bi_2Se_3 surface single crystal correspond not only the purpose of calibration of AFM; it also can be used for calibration of STM and checking both the sharpness of STM tips and the quality of conducting cantilevers. Thus, the Bi_2Se_3 single crystal, which contains a smaller amount of lattice defects in comparison with HOPG, broadly used by researchers [27], can serve its full analogue and, due to its more perfect structure, can be used by researchers as a calibration standard.

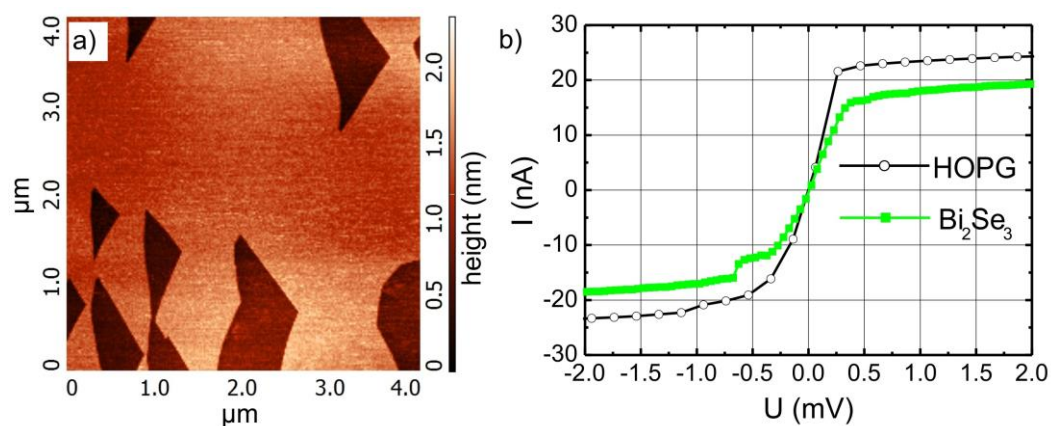


Figure 8. (a) STM image of a freshly cleaved (0001) Bi_2Se_3 surface. (b) Comparative graph of current-voltage characteristics measured with the use of a conductive AFM probe in contact mode on the surface of Bi_2Se_3 and HOPG. This graph demonstrates near-identical surface conductivities of the two materials.

4. Conclusions

Freshly cleaved (0001) Bi_2Se_3 and (010) ZnWO_4 surfaces of high-quality single crystals offer step-height standards appropriate for calibrating scanning probe microscopes (STMs). Moreover, the conducting surfaces of Bi_2Se_3 crystals offer height measures appropriate for calibrating STMs and for testing conductive SPM probes. Easy cleavage of Bi_2Se_3 and ZnWO_4 crystals permits making fresh surface of the measure prior to SPM calibration and allows protection of the SPM probe from contaminations during calibration. The crystal cleaving process can be repeated many times due to the fact that the thickness of the layer being detached normally amounts to several micrometer parts, and the calibration measure has a thickness of three to five millimeters. The inter-relation between the cleaving method and the degree of smoothness of the formed (0001) Bi_2Se_3 surface was clarified. Atomically smooth surfaces having no steps on areas larger than $400 \mu\text{m}^2$ were obtained. High stability of the (0001) surface of Bi_2Se_3 , whose morphology exhibited no changes over a period of six months, was confirmed. The (010) surface of ZnWO_4 crystals remained atomically smooth during one day, but already two days later an additional nanorelief of amplitude $\sim 0.3 \text{ nm}$ appeared on this surface. This relief, however, did not further grow in height, and it did not hamper the calibration. Stable surfaces guarantee high accuracy even when additional calibrations of SPM are carried out under ambient conditions. Simplicity and the possibility of quick fabrication of the step-height standards, as well as their high stability, make these standards available for many workers, first of all, for a great, permanently growing number of users involved in 3D printing activities.

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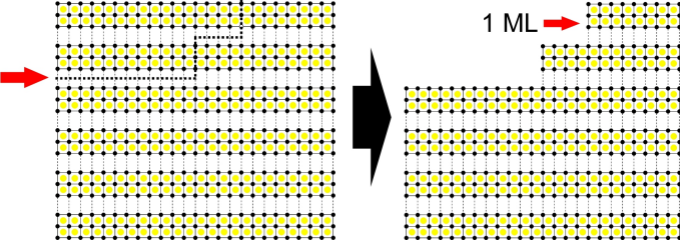
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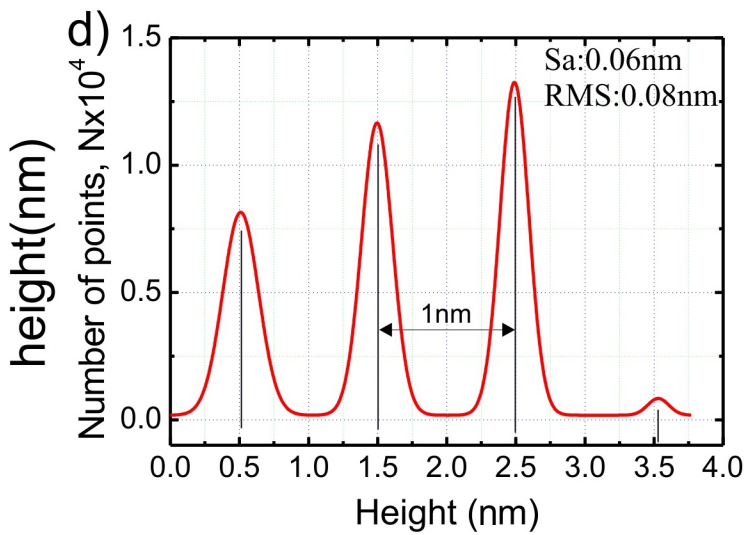
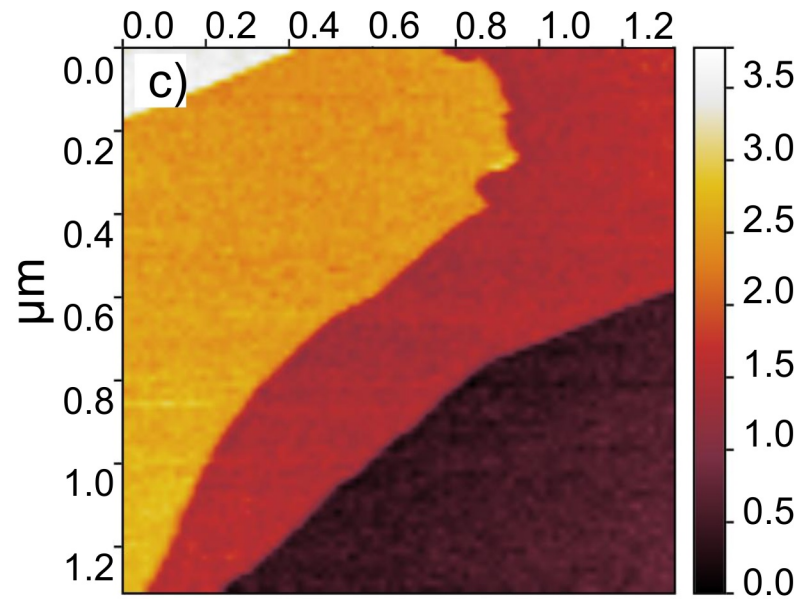
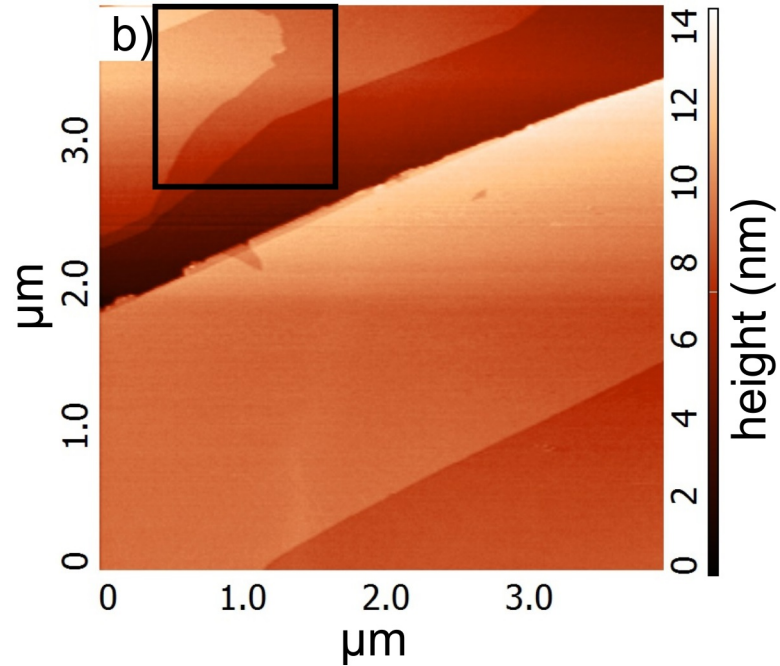
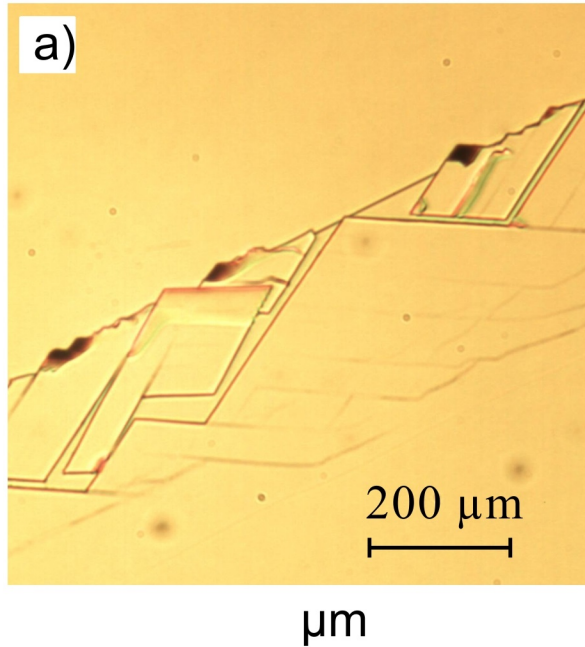
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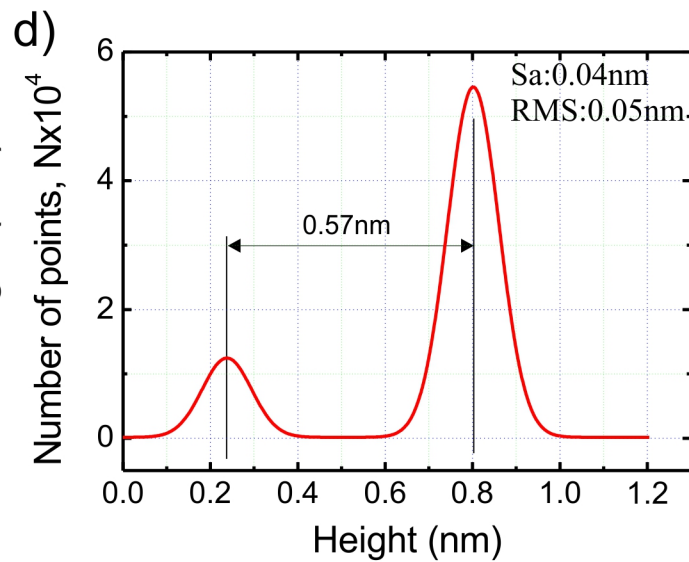
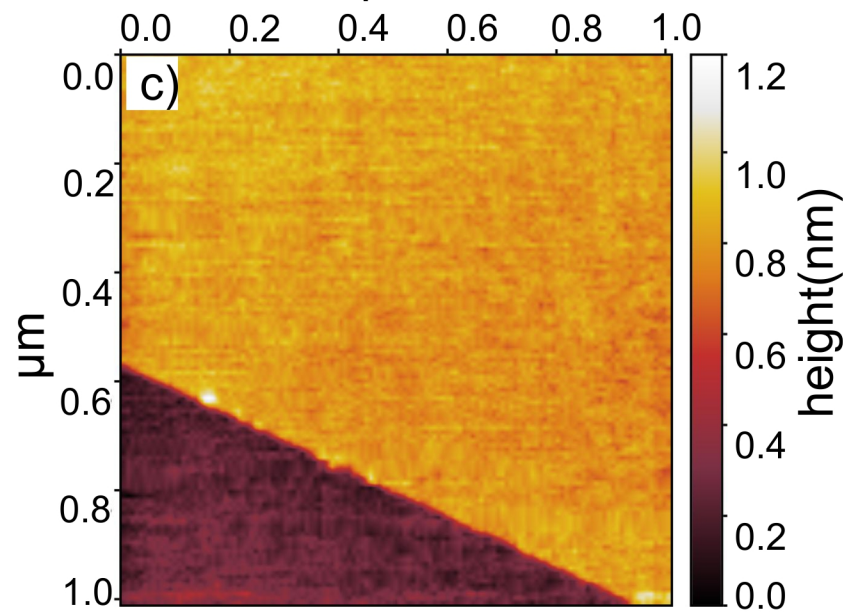
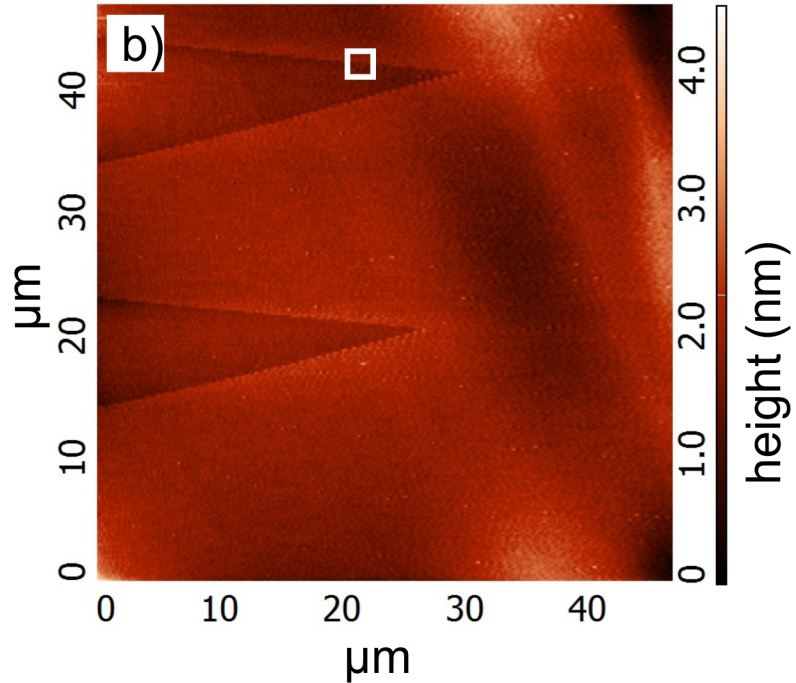
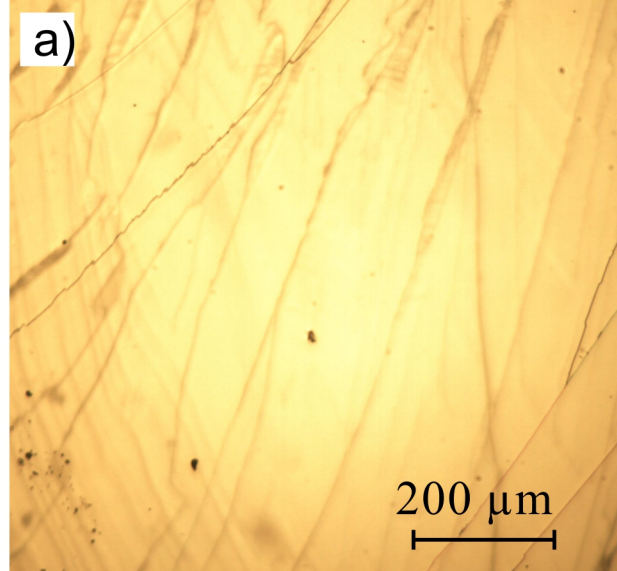
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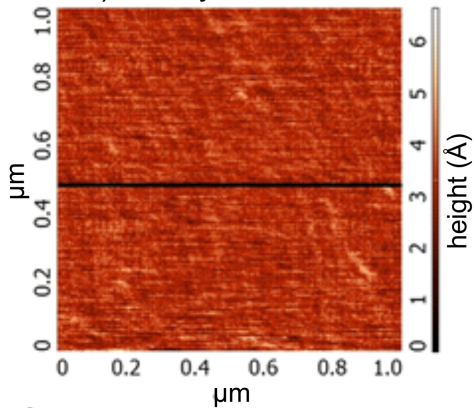
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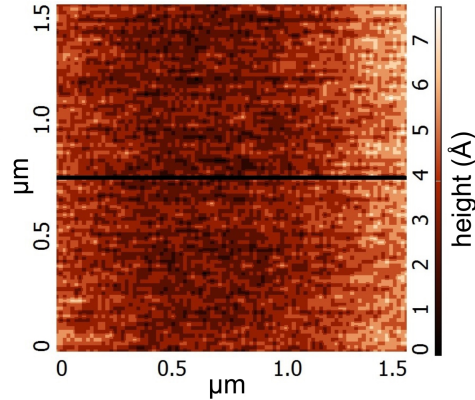




a) freshly cleaved



b) after 1 week



c) after 6 months

