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Investigation of (100) In_4Se_3 crystal surface nanorelief

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The crystallography and topography of the (100) cleavage surfaces of layered semiconductor In_4Se_3 crystal have been studied by low energy electron diffraction (LEED), scanning tunnelling and atomic-force microscopy (STM, AFM) in ultrahigh vacuum (UHV). The structure of surface LEED patterns, shape and dimensions of subsequent STM- and AFM-profiles agree well with the lattice parameters derived from the bulk crystal structure obtained by X-ray diffraction. The local density of states and band gap for (100) In_4Se_3 have been obtained by scanning tunnelling spectroscopy and point to the same integral gap value as for bulk crystal. The STM/STS results evidence the stability of interlayer cleavage surface and confirm that anisotropic striated low conductive cleavage surfaces might be suitable as matrices/templates in formation of surface nanowires or nanostructures.

Кристаллография и топография поверхностей (100) скалывания кристаллов слоистых полупроводников In_4Se_3 исследованы методами дифракции медленных электронов (ДМЭ), сканирующей туннельной и атомно-силовой микроскопий (СТМ, АСМ) в сверхвысоком вакууме. Структура рефлексов ДМЭ, форма и характерные размеры в полученных СТМ- и АСМ-профилях поверхностей скалывания хорошо согласуются со структурой и параметрами решетки, полученными для кристаллов In_4Se_3 орторомбической структуры методом рентгеновской дифракции. Локальная плотность электронных состояний и ширина запрещенной зоны для поверхностей скалывания (100) In_4Se_3, полученная методом сканирующей туннельной спектроскопии, указывают на ее интегральное значение, такое же как для объемных кристаллов. Результаты ДМЭ, СТМ/АСМ указывают на стабильность междуслоевых поверхностей скалывания и перспективность использования слабо проводящих бороздчатых анизотропных сколов в качестве матриц/шаблонов для формирования поверхностных нанопроволок или наноструктур.

The structure of In_4Se_3 layered semiconductor crystal is described as close-packed layers, each containing a complex In–Se bindings, with a weak van der Waals interaction between the layers [1]. The latter fact allows to provide perfect cleavage surfaces, particularly in ultrahigh vacuum (UHV) [2]. The striking feature of In_4Se_3 (100) surface is a furrowed and chainlike anisotropic relief as one could suggest after inspection of bulk crystal and energy structure [3]. This 2D-like (100) cleavage surface of layered In_4Se_3 crystals attract a great attention due to its potential utilization as template for preparation of nanometer scale devices, e.g. nanowires [2, 4]. In this work,

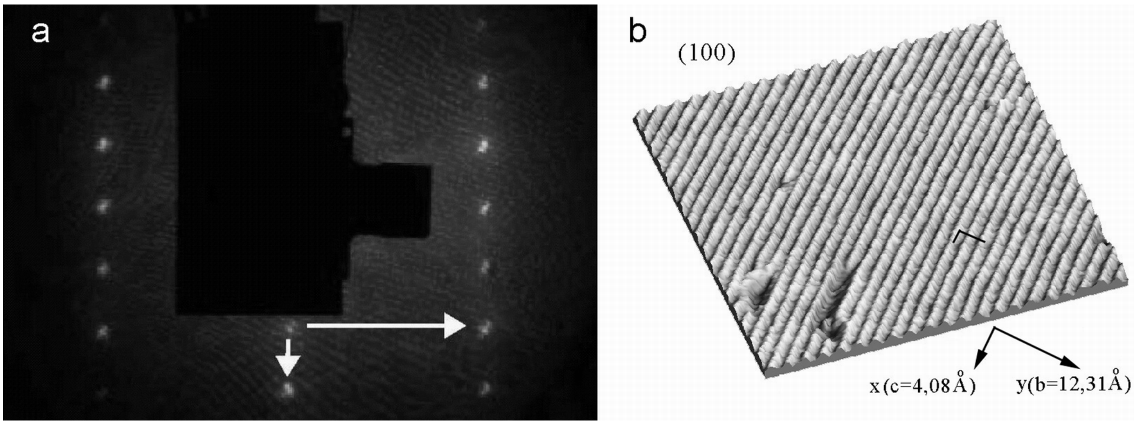

Fig. 1. a) LEED pattern at 76 eV from (100) In_4Se_3 UHV cleavage ($\mathbf{b}^*$ (shorter) and $\mathbf{c}^*$ (longer) being the reciprocal lattice constants); b) 3D STM image of In_4Se_3 (100) structure fragment (36×36 nm^2) showing chains along the x (**c**) direction. STM-image obtained under bias voltage V = 2 V and tunneling current I_t = 150 pA.

we employed the low energy electron diffraction (LEED), scanning tunneling and atomic force microscopy (STM, AFM) and the scanning tunneling spectroscopy (STS) to study the UHV (100) In_4Se_3 cleavages.

The studied In_4Se_3 layered crystals (3×6×4 mm^3 samples of a convenient shape for cleavage *in situ*) have been grown by Czochralski method. In all LEED, STM/STS, and AFM studies, the samples were cleaved *in situ* at room temperature in a UHV chamber using a low profile stainless steel microtome blade (LEED) and stainless steel tip (STM/STS, AFM). An Omicron NanoTechnology STM/AFM System with UHV atmosphere ($3 \cdot 10^{-11}$ Torr) was applied. The STM/STS of (100) In_4Se_3 was carried out yielding topography, I–V, dI/dV, and normalized dI/dV vs V dependences. The STM topography images were obtained in constant tunneling current mode. The AFM images were obtained in constant force contact mode with application of Si cantilever, using a minimum contact force (up to 3–6 nN) to avoid damaging the crystal surface. To visualize the measured STM and AFM data, the computer program WSxM v.2.2 designed by Nanotec Electronica (WSxMc; http://www.nanotec.es) was applied.

The cleavages obtained in UHV and in air just before introducing into UHV ("fresh" ones) reveal periodic furrowed structures well comparable with lattice constants derived from X-ray diffraction (XRD). The surface order of (100) In_4Se_3 was established by LEED and STM (Figs. 1–3) and AFM (Fig. 4). The surface order of (100) In_4Se_3 cleavages in LEED experiment was also reported in [5]. The surface structure is stable and does not change under cleavage and exposure in UHV [6]. On the whole, the surface pattern varies slightly over the entire studied area, but examined Fourier filtered images disclose consistent periodical patterns. The measured lattice constants of the surface crystal structure by LEED, STM and AFM are in agreement with the bulk lattice constants obtained by XRD x = 4.0810(5) Å (along **c** direction parallel to furrowes), y = 12.308(1) Å (along **b** direction normal to furrows or chains), in the orthorhombic space group P_{nnm} (Fig. 4b).

Some surface properties of (100) In_4Se_3, $In_4Se_3(Cu)$ crystals were studied in [2, 7]. Scanning electron microscopy, STM surface micro- and nanostructure, and X-ray photoelectron spectra were obtained for interfaces on the cleavages that have been exposed in air. The new electron interactions have been observed for these surfaces. The formation of In–In metallic (on fresh and old cleavages) and In–O oxidized (for old cleavages) bindings and, consequently, metallic and oxidized phases on the (100) surfaces of In_4Se_3, and Cu–In–Se bindings for intercalated $In_4Se_3(Cu)$ crystals (Cu $2p_{3/2}$, In $3d_{5/2}$, Se $3d$ binding energies are close to ones for $CuInSe_2$) have been found. Therefore, it is of interest to study not only probability of phase inhomogeneity of (100) In_4Se_3 cleavages *in situ*, but also the surface local density of states LDOS — $N_S(E)$ and local energy structure by STM/STS methods.

The STS combined with STM is a very powerful tool to study the local variations of electronic states (LDOS). During the STM

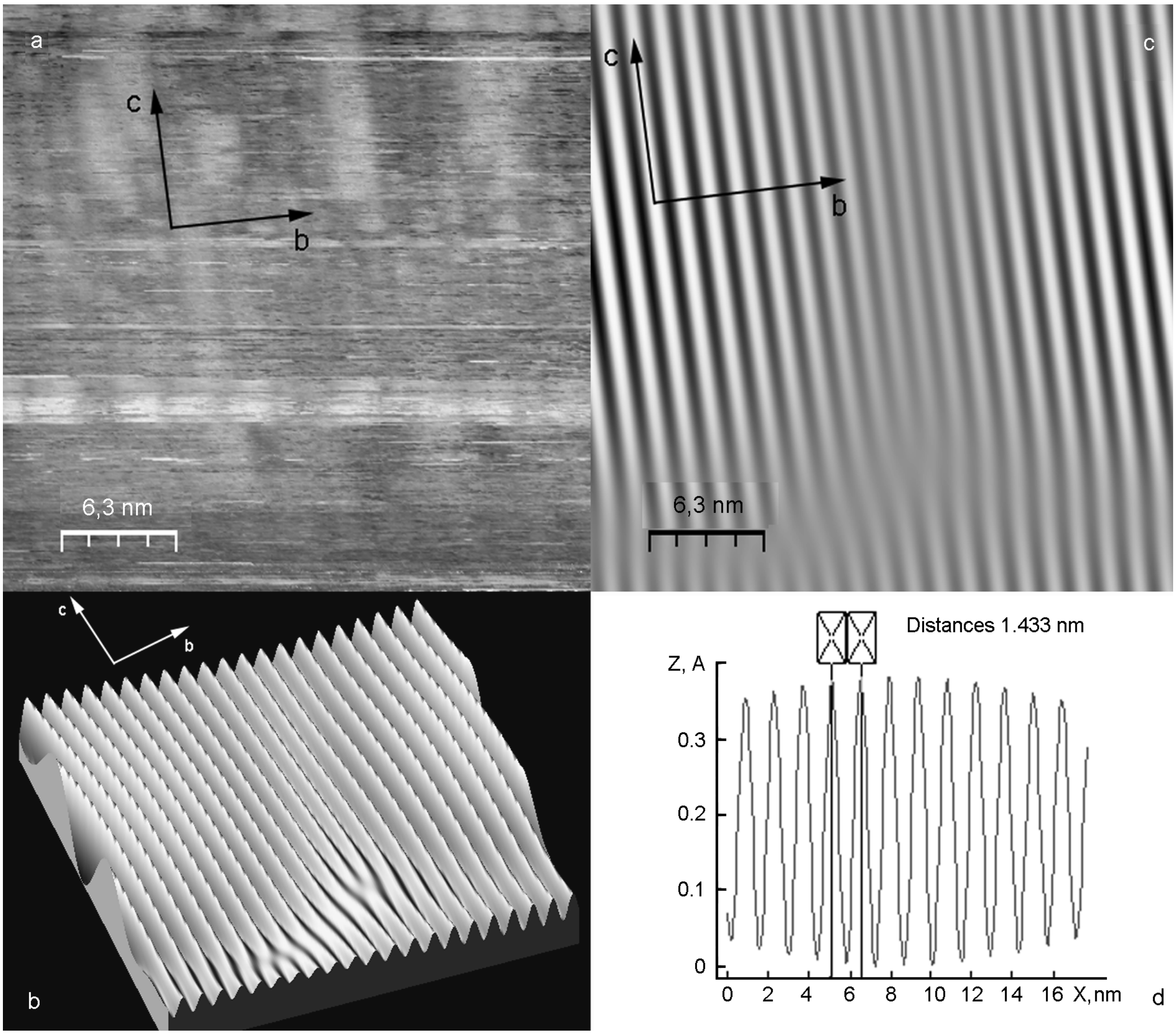

Fig. 2. STM results: a) Constant current STM image of 30×30 nm^2 In_4Se_3 (100) UHV cleavage surface; b, c) Corresponding 2D and 3D FFT images; d) Measured periodical distances along **b** axis on 2D FFT profile.

imaging, the scanning tip is briefly stopped to record local tunneling spectra ($dI_t(V)/dV = f(V)$); the tip is then scanned again to continue the imaging process. By repeating those operations, it is possible to obtain a topographic image and numerous local tunneling spectra with measurement locations being specified in the image [6]. If the atomic resolution is attained in the STM imaging, the local tunneling spectra are atomic site sensitive (Fig. 3). The STS result can also be expressed as a spatial map of $dI_t(V)/dV$ at fixed V — a "conductance map". The latter is thought to be a real-space representation of band structure, traditionally understood in momentum space [6]. It is evident that the real-space investigations of band structures provide particularly useful information regarding the results of (100) In_4Se_3 surface studies [2–6], because they are closely related with the local electron structure on atomic scale.

The perfect crystal cleavage structure is found through the macroscopic sample area as confirmed by LEED patterns. The LEED and STM results of the In_4Se_3 cleavages show an unrecon-structed (100) surface structure. Fig. 2 shows the constant current STM image of 30×30 nm^2 In_4Se_3 (100) UHV cleavage surface and corresponding 2D and 3D Fourier Fast Transform (FFT) images as well as the measured periodical distances along **b** axis of the 2D profile. The measured lattice constants of the surface crystal structure (see Fig. 2d) are in agreement with the bulk lattice constant $y = 12.308(1)$ Å along **b** direction normal to furrows or chains.

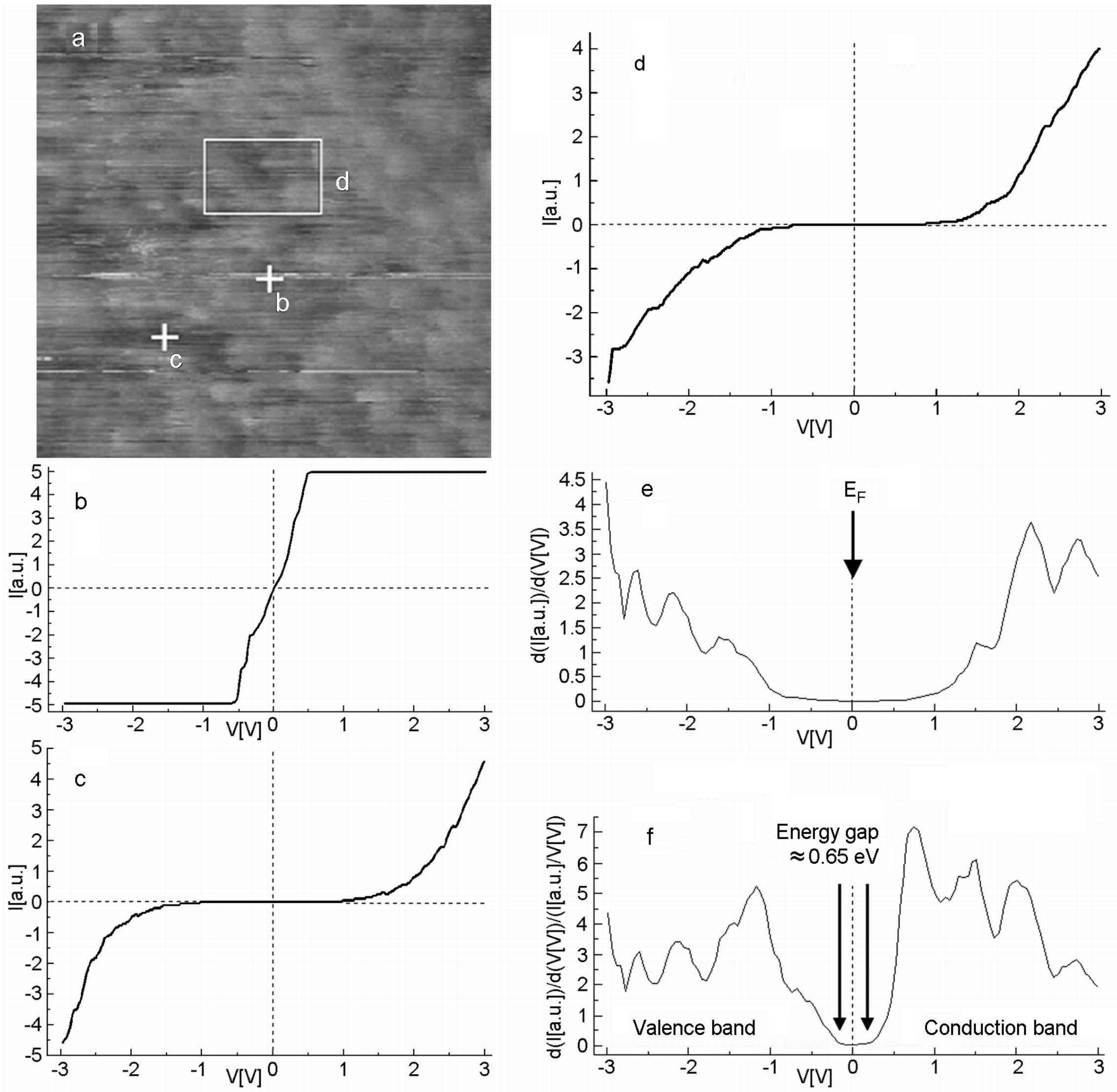

Fig. 3. STM/STS study of the (100) In_4Se_3 UHV cleavage surface: a) STM 50×50 nm^2 image area; (b, c) — local $I = f(V)$ curves measured at individual points within 50×50 nm^2 image: b) I–V metallic behavior in point marked by cross in Fig. 3a (metallic fragment); c) semiconducting one; d) typical I–V curves averaged over highlighted rectangular area in Fig. 3a (spatially averaged $I = f(V)$ curves for 100 points); e) differential spatially averaged dI/dV spectra; f) normalized dI/dV spectra.

STM/STS results show a local energy and phase inhomogeneity of (100) In_4Se_3 *in situ* cleavages (see Figs. 2, 3). Some points of the surface (about 10 Å size) show metal-like I_t–V characteristics (Fig. 3b). The isolated nanosize regions were found to exhibit a metal behavior. The above results can be considered to be caused by presence of non-stoichiometric indium (In) on the cleavages that precipitates into interlayer spaces as a result of the crystal self-intercalation with indium. However, averaging over small areas (see rectangle in Fig. 3a) gives I_t–V characteristics inherent in semiconductor (Fig. 3d). Thus, the widening of the studied area results into change of tunneling behavior from metallic to semiconducting that is characterized by increasing non-linearity of I_t–V curves. Differential spatially averaged dI_t/dV spectra vs bias voltage V ($dI_t(V)/dV = f(V)$) are a function of energy and proportional to the LDOS — $N_S(E)$.

Using the STS, the band gap value has been determined as 0.65 eV that indicates the overall semiconducting nature of (100) In_4Se_3 surface. It is possible also to reveal the presence of the surface states within the band gap (Fig. 3). The gap value $E_g \cong 0.65$ eV for In_4Se_3 (n-type conductivity,

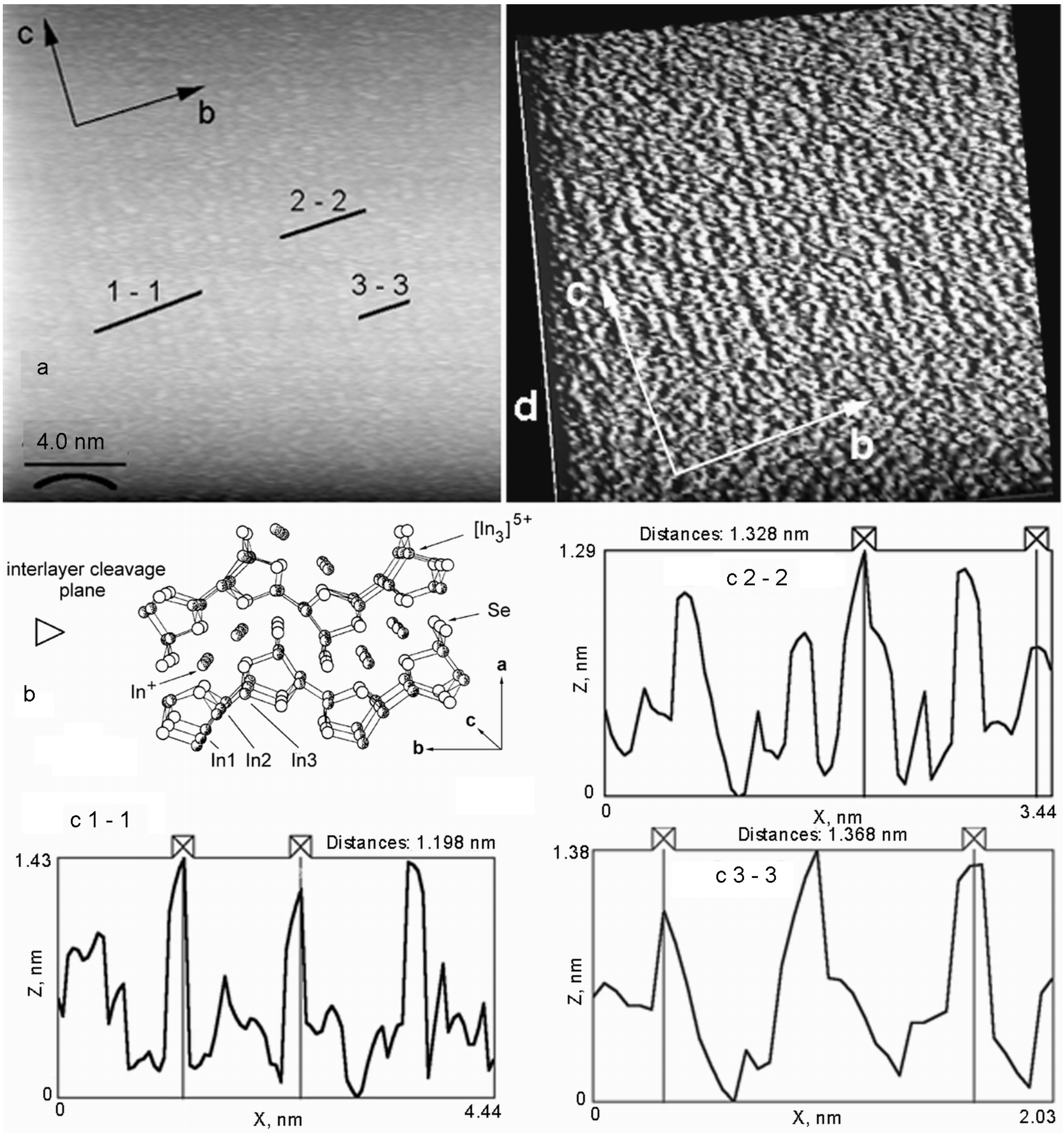

Fig. 4. a) AFM image of 20×20 nm^2 region of the (100) In_4Se_3 UHV cleavage surface; b) In_4Se_3 structure fragment [4] (projection on (001) plane). Triangle shows the cleavage direction. $[In_3]^{5+}$ is the indium polycation (In1, In2, In3); In^+ is the indium cation (In4). Cleavage plane (100) is normal to the crystal growth axis **a**; c) profiles obtained along the corresponding traces on the AFM image. Markers indicate typical distances in the periodic surface structure; d) 3D AFM image.

$n \cong 5\cdot10^{15}-10^{17}$ cm^{-3}, at 300 K), obtained using STS results, agrees satisfactory with $E_g \cong 0.62-0.67$ eV values for bulk In_4Se_3 layered semiconductor crystal, obtained by other experimental and theoretical methods [8, 9]. In particular, this similarity correlates with the stability and lack of reconstruction at the (100) In_4Se_3 surface structure under cleavage and UHV exposure.

The AFM allows one to obtain a high, both lateral and height resolution for semiconductor surfaces enough flat on the atomic scale [10]. We have applied the 2D AFM images of In_4Se_3 cleavages to characterize quantitatively the (100) surface morphology. Fig. 4a shows a 20×20 nm^2 AFM topography of (100) In_4Se_3 crystal surface, obtained by cleavage in UHV. This 2D image displays a periodical furrowed-chain-like structure which corresponds to the surface crystal lattice. The furrows are parallel to **c** axis and normal to **b** axis (see the crystal structure fragment in Fig. 4b). To determine the periods of such a surface structures, the line traces profiling was carried out along **b** and **c** directions. Fig. 4c shows the profiles of such a furrowed-chain-like structure obtained along **b** axis. It is known that data obtained directly from AFM images overestimate lateral dimensions, because the obtained image is a combination of the tip and sample interactions. Thus, the tip broadening effect and errors of surface roughness measurements are typical for AFM images. In our case, however, the obtained images are acceptable. They contain most features of the (100) In_4Se_3 surface structure being confirmed by XRD. For each profile, the presented periodical distances are in satisfactory agreement with the **b** value of 12.3 Å. However, the analysis of AFM profiles along **c** direction failed to give a clear periodicity, evidently due to the insufficient resolution.

Fig. 4d shows a 3D view of the same surface. The furrowed (100) In_4Se_3 cleavage structure could be clearly seen here and there at the studied area. However, the clearness of periodic features that represent the furrowed structure of the (100) In_4Se_3 UHV cleavage surface is rather poor. The signal-to-noise ratio is minor. Thus, besides of profiling the AFM images for the UHV cleavages, with the **b** and **c** surface lattice dimensions analysis, we have tried a two-dimensional FFT filtering. When the AFM images for the UHV cleavages were transformed into the Fourier space making use of 2D FFT, a consistent pattern of periodicities was observed. In both unfiltered and, more defined, filtered AFM images the furrowed structure of the cleavage surface can be seen, resolving also the elevated In atoms in position In4 (In^+).The AFM images were also obtained from the (100) In_4Se_3 surfaces cleaved in air, so-called "fresh" cleavages. Fig. 5a shows the corresponding 20×20 nm^2 2D AFM image. Such images are more noisy than those from the *in situ* cleavages, and 2D FFT images (Fig. 5b) reveal a periodical structure, however, with a dilated period of ~16 Å. Such changes are related evidently to adsorbate coverage of the cleavage surface [10, 11] and changes in tip-sample surface interaction [10].

Thus, when studying the (100) cleavage surfaces of In_4Se_3 layered semiconductor crystals, the **l** periodic furrowed structures have been revealed commensurable with the lattice constants determined using X-ray diffraction. The LEED, STM, AFM results confirm that (100) In_4Se_3 furrowed and chainlike surface structure is stable and is non reconstructed under the cleavage and UHV exposure and might be suitable as anisotropy low conductive matrix/template to obtain the conductive surface nanowires or

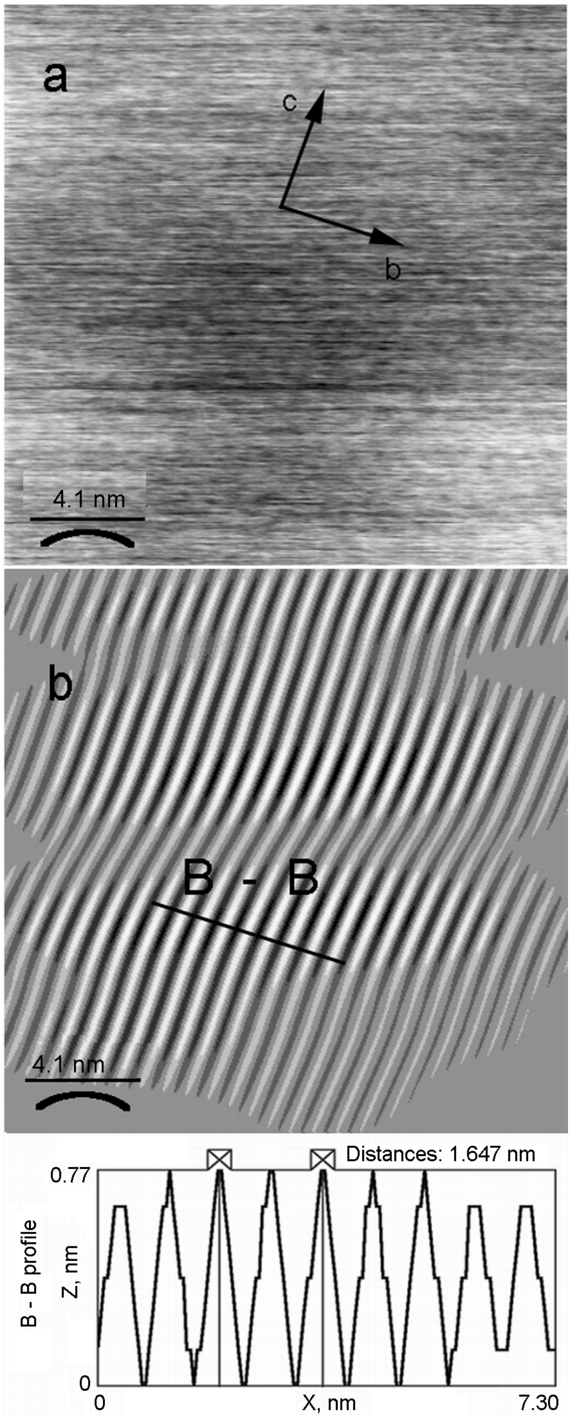

Fig. 5. a) 20×20 nm^2 AFM image of "fresh" cleavage surface of (100) In_4Se_3 crystal; b) corresponding 2D FFT image for "fresh" cleavage. Profile is obtained along corresponding trace on the 2D FFT image. Markers indicate typical distances in the periodic surface structure.

nanostructures. The STM/STS results show a local energy and phase inhomogeneity of (100) In_4Se_3 cleavage surfaces at atomic scale. The LDOS and band gap for (100) In_4Se_3 have been obtained by STS and gave integrated gap value the same as for the bulk crystal.

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Дослідження нанорельєфу поверхонь (100) кристалів In_4Se_3

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Кристалографію та топографію поверхонь (100) сколювання кристалів шаруватих напівпровідників In_4Se_3 досліджено методами дифракції повільних електронів (ДПЕ), скануючої тунельної та атомно-силової мікроскопій (СТМ, АСМ) у надвисокому вакуумі. Структура рефлексів ДПЕ, форма і характерні розміри в одержаних СТМ- та АСМ-профілях поверхонь сколювання відповідають структурі і параметрам гратки, одержаним для кристалів In_4Se_3 орторомбічної структури методом ренгенівської дифракції. Локальна густина електронних станів і ширина забороненої зони для поверхонь сколювання (100) In_4Se_3, що отримані методом скануючої тунельної спектроскопії (вказують на її інтегральну величину, таку ж як для об'ємних кристалів. Результати ДПЕ, СТМ/АСМ вказують на стабільність міжшарових поверхонь сколювання та перспективність використання слабкопровідних борознистих анізотропних сколів як матриць/шаблонів для формування поверхневих нанодротів та наноструктур.