ВІСНИК ЛЬВІВ. УН-ТУ *VISNYK LVIV UNIV.*
Серія фіз. 2009. Вип. 43. С. 28–35 *Ser. Physics. 2009. Is. 43. P. 28–35*

УДК 537.533.2
PACS number(s): 68.37.Ps; 68.47.Fg; 68.35.bg

NANOSCALE STM/STS/AFM STUDIES OF (100) In_4Se_3 CRYSTAL SURFACES

P. Galiy[1], T. Nenchuk[1], O. Dveriy[1], A. Ciszewski[2], P. Mazur[2], S. Zuber[2]

[1]*Electronics Department, Ivan Franko Lviv National University, 50 Dragomanov Street, Lviv, 79005, UKRAINE*
[2]*Institute of Experimental Physics, University of Wroclaw, Pl. Maxa Borna 9, Wroclaw, 50-204, POLAND*
e-mail: galiy@electronics.wups.lviv.ua

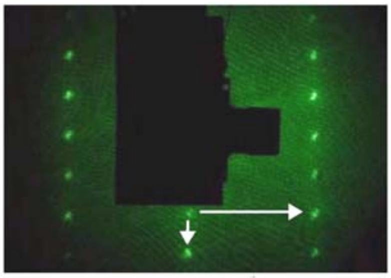
The crystallography and topography of the (100) cleavage surfaces of layered semiconductor In_4Se_3 crystal was analysed by low energy electron diffraction (LEED), scanning tunnelling and atomic force microscopy (STM, AFM) in ultrahigh vacuum (UHV). The "structure" of surface LEED patterns, shape and dimensions of subsequent STM- and AFM-profiles well correspond to the lattice parameters derived from bulk crystal structure obtained by X-ray diffraction (XRD). The local density of surface states and band gap for (100) In_4Se_3 have been obtained by scanning tunnelling spectroscopy (STS) and gave gap value the same as for bulk crystal. Our studies confirm that (100) In_4Se_3 surface structure is stable and non reconstructed under the cleavage and might be suitable for surface nanowires fabrication.

Key words: low-dimensional structures; layered semiconductor surface; low energy electron diffraction; scanning tunnelling microscopy and spectroscopy; atomic force microscopy.

2D layered crystals have received great attention, due to their potential utilization as templates for device fabrications on a nanometer scale, e.g. nanowires [1, 2]. The structure of In_4Se_3 layered semiconductor crystal is described as a close-packed layers, each containing a complicated In-Se bindings, with a weak van der Waals bonding between the layers. The last one allows to have a perfect cleavages surface, particularly in UHV conditions. The striking feature of In_4Se_3 (100) surface might be furrowed and chainlike relief as one could suggest after inspection of bulk crystal structure. In present work, we employed the low energy electron diffraction (LEED), scanning tunneling and atomic force microscopy (STM, AFM) and the scanning tunneling spectroscopy (STS) for study of the ultrahigh vacuum (UHV) (100) In_4Se_3 cleavages.

In_4Se_3 layered crystals have been grown by Czochralski method. The Omicron NanoTechnology STM/AFM System with ultrahigh vacuum atmosphere (3×10^{-11} Torr) at room temperature was applied. The STM/STS of (100) In_4Se_3 has been carried out yielding topography, I–V, dI/dV and normalized dI/dV versus V. STM topography images were collected in contact current mode. The AFM images were collected in contact constant force 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 we applied the computer program WSxM v.2.2 designed by Nanotec Electronica (WSxM© ; http://www.nanotec.es).

LEED, STM/STS study. The cleavages obtained in UHV and in the air just before introducing in the UHV ("fresh" ones) reveal periodic furrowed structures purely 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, 2) and AFM (fig. 4). The surface structure is stable and non-reconstructed under cleavage and exposure in UHV [3]. On the whole, the surface pattern is slightly variable 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 of $x = 4{,}0810(5)$ Å (along ***c*** direction parallel to furrows), $y = 12{,}308(1)$ Å (along *b* direction normal to furrows or chains), in the orthorhombic space group P_{nnm}, obtained by XRD (fig. 4, *b*).



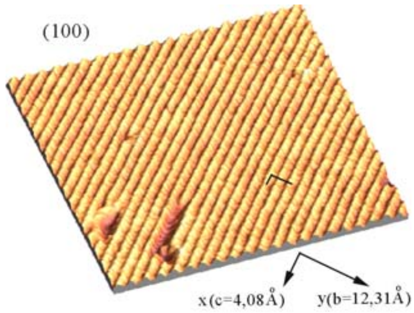


Fig. 1. *a* – LEED pattern at 76 eV from (100) In_4Se_3 UHV cleavage (b^* (shorter) and c^* (longer) - the reciprocal lattice constants); *b* – 3D-view STM image of In_4Se_3 (100) structure fragment (36×36 nm^2) shows chains along the *x* (*c*) direction. STM-image obtained under V_b=2 V and tunneling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

The excellent 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 unreconstructed (100) surface structure. The 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 and also measured periodical distances along *b* axis on 2D profile. The measured lattice constants of the surface crystal structure (see fig. 2, *d*) are in agreement with the bulk lattice constants of $y = 12{,}308(1)$ Å – along *b* direction normal to furrows or chains.

STM/STS results show on local energetic and phase non-homogeneity of (100) In_4Se_3 cleavages *in situ* (see figs. 2, 3). Some points on the surface (with size ≅ 10 Å) show I_t-*V* metal like characteristics (fig. 3, *b*). The isolated nano regions were found to exhibit metallic behavior. However, averaging by small areas (see rectangular on fig. 3, *a*) gives I_t-*V* semiconductor characteristics (fig. 3, *d*). The above results might be discussed in terms of presence of the non stoichiometric indium (In) on the cleavages that precipitates into interlayer spaces as the result of intercalation.

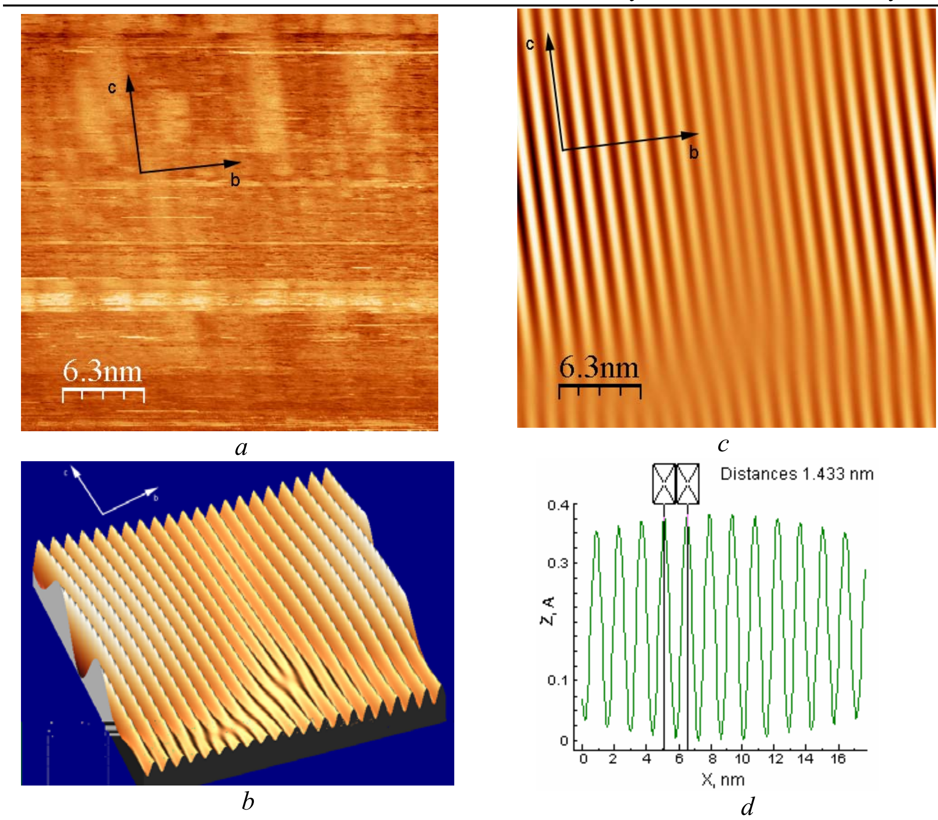


Fig. 2. STM results: *a* – Constant current STM image of 30×30 nm^2 In_4Se_3 (100) UHV cleavage surface; *b*, *c* – Corresponding 2D and 3D FFT images; *d* – measured periodical distances along *b* axis on 2D FFT profile

The widening of the studied area results into change of tunneling behavior from metallic to semiconducting as characterized by increase in I_t–V plots non-linearity. Differential spatially averaged dI_t/dV spectra versus voltage bias V $(dI_t(V)/dV = f(V))$ are the function of energy and proportional to the local density of surface states (LDSS) – $N_S(E)$. Obviously, the tunneling current I_t is equal

$$\mathrm{I_t} \propto \exp(-\alpha S\sqrt{\Phi}) \times \int_0^{eV} N_s(E)dE \cong \exp(-\alpha S\sqrt{\Phi}) \times N_s(E) \times \mathrm{eV}$$

therefore

$$dI_t / dV \propto N_s(E)\,,$$

and for V=0 corresponding $N_S(E_F)$ gives LDSS near the Fermi level. The STS derived the band gap value ~0,65 eV that indicates on the overall semiconducting nature of (100) In_4Se_3 surface and one might reveal the presence of the surface states in the band gap (fig. 3). The obtained gap value E_g=0,65 eV for In_4Se_3 (*n*-type conductivity, $n \cong 5\times10^{15}$-10^{17} cm^{-3}, at 300 K), as STS result, satisfactory agrees 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 [4–6]. Particularly, this similarity correlate with the stability and lack of reconstruction at the (100) In_4Se_3 surface structure under cleavage and exposure in UHV.

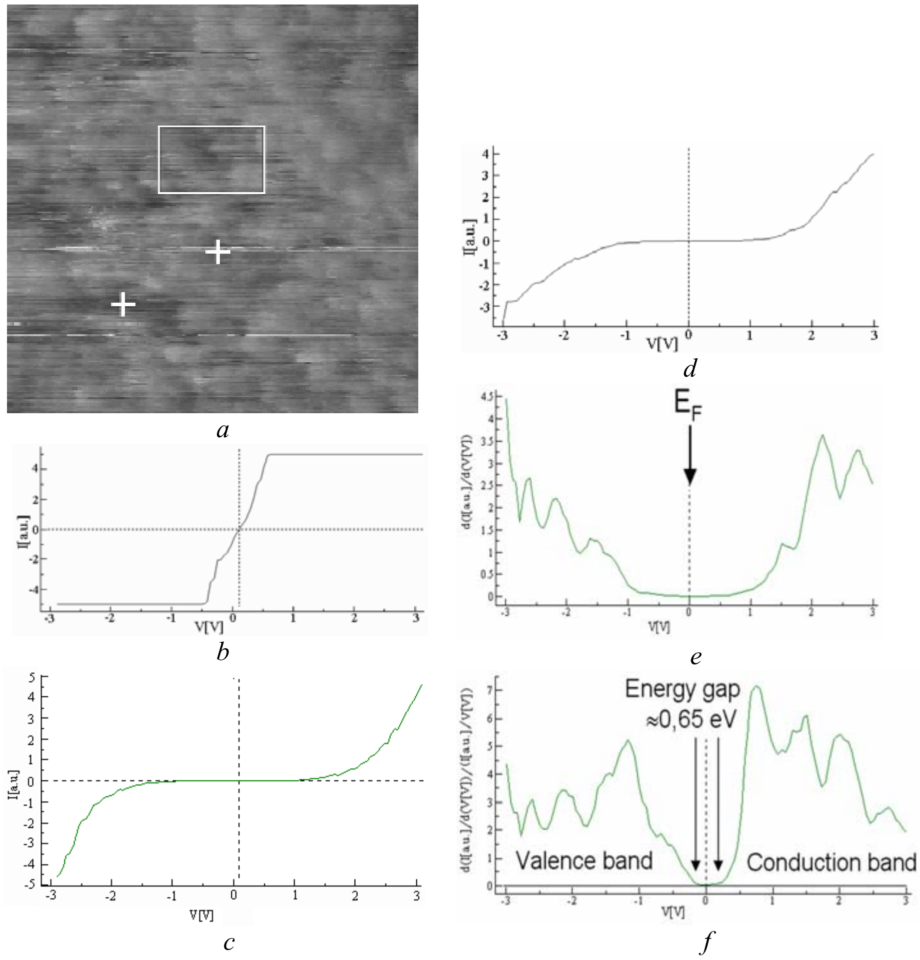
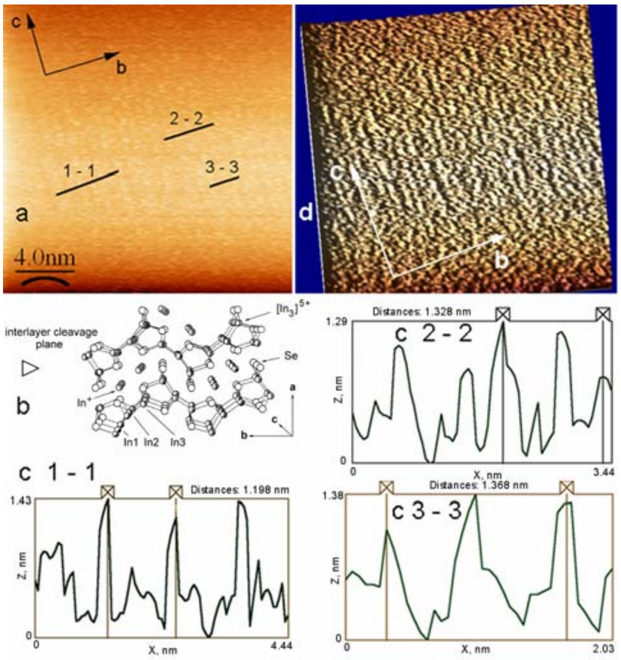


Fig. 3. STM/STS study of the (100) In_4Se_3 UHV cleavage surface: *a* – STM 50×50 nm^2 image area; *b*, *c* – Local $I = f(V)$ curves measured at individual points within 50×50 nm^2 image: *b* – *I-V* metallic behavior in point marked by cross on *a* – (metallic fragment); *c* – semiconducting one; *d*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

Atomic Force Microscopy (AFM). The AFM studies allow one to obtain a high, both lateral and height resolution for enough flat on the atomic scale semiconductor surfaces. We applied the 2D AFM images of In_4Se_3 cleavage surfaces for quantitative characterization of the (100) surface morphology. fig. 4a shows a 20×20 nm^2 AFM topography of (100) In_4Se_3 layered crystal surfaces, obtained by cleavage in UHV.

This 2D image appears with a periodical furrowed-chainlike structure, which corresponds to the surface crystal lattice. The furrows are parallel to ***c*** axis and normal to *b* axis (see the fragment of crystal structure in fig. 4, *b*). In order to check the periods for such surface structures, the line traces profiling was carried out along *b* and *c* direction. Fig. 4, *c* shows the profiles of such a furrowed-chainlike structure, obtained along *b* axis. It is known that data obtained directly from AFM images overestimates lateral dimensions, because the obtained image is a combination of the tip and sample interactions.



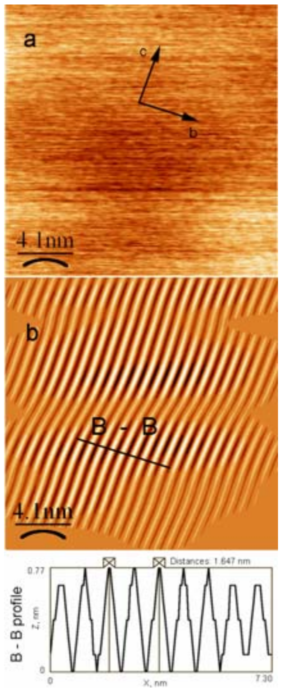


Fig. 4. *to the Left (a, b, c, d)*: *a* – AFM image of 20×20 nm^2 region of the (100) UHV cleavage surface of In_4Se_3 crystal; *b* – In_4Se_3 structure fragment [2] (projection on (001) plane). Triangle shows the cleavage direction. $[In3]^{5+}$ is the polycation of indium (In1, In2, In3); In^+ is the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

Fig. 5. *to the Right (a, b)*: *a* – 20×20 nm^2 AFM image of (100) “fresh” cleavage surface of In_4Se_3 crystal; *b* – corresponding 2D FFT image for “fresh” cleavage. Profile as obtained along corresponding trace on the 2D FFT image. Markers indicate typical distances in the periodic surface structure

The tip broadening effect and incorrectness of surface roughness measurements are obvious for AFM images. In our paper, however, the obtained images are acceptable. They contain most features of the (100) In_4Se_3 surface structure, which is confirmed by X-ray diffraction. For each profile, the presented periodical distances are in satisfactory agreement with the *b* value 12,3 Å. However, the analysis of AFM profiles along *c* direction failed to give a clear periodicity, evidently due to the resolution.

Fig. 4d shows a 3D view of the same surface. The furrowed (100) In_4Se_3 cleavage structure could be clearly seen in some places of the studied area. However, the clarity of the periodic features that represent the furrowed structure of the (100) In_4Se_3 UHV cleavage surface is poor. The signal-to-noise ratio is minor. Thus, besides 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 collected from the (100) In_4Se_3 surfaces, as inserted after the cleavage in the air, so-called "fresh" cleavage. Fig. 5, *a* 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. 5, *b*) reveal a periodical structure, however, with a dilated period of ~16 Å. Evidently, such changes are related to adsorbate coverage of the cleavage surface [2, 8] and changes in tip-sample interaction.

We applied LEED, STM, AFM to obtain the lattice resolution of the cleavage surfaces of In_4Se_3 layered semiconductor crystal and STS to get surface local electron-energetic structure and quality characteristics of density of the states. The cleavages obtained in UHV and in the air just before introducing into the UHV chamber reveal periodic furrowed structures purely comparable with the lattice constants derived from X-ray diffraction.

The local density of surface states and band gap for (100) In_4Se_3 have been obtained by STS and gave gap value the same as for the bulk crystal. The last one also confirms that (100) In_4Se_3 structure is stable – non reconstructed under the cleavage and exposure in UHV and might be suitable for fabrication of surface nanowires.

On the whole, the observed surface pattern is slightly variable over the entire studied surface, but the examined Fourier filtered images disclose consistent periodical patterns, however, with an increase of the dilated period normal to the chains from UHV to "fresh" cleavages.

The surfaces, containing adsorbates and amorphous interface, don't reveal any surface periodicity.

1. *Galiy P.V., Musyanovych A.V., Fiyala Ya.M.* The Interface Microscopy and Spectroscopy on the Cleavage Surfaces of the In_4Se_3 Pure and Copper Intercalated Layered Crystals // Phys. E: Low-dimensional Systems and Nanostructures. 2006. Vol. 35. N 2. P. 88–92.
2. *Galiy P.V., Nenchuk T.M., Lozovyj Ya.B., Fiyala Ya.M.* Structural and energy changes at the cleavage surfaces of In_4Se_3 layered crystals under interface formation // Funct. Mat. 2008. Vol. 15. N 1. P. 68–73.
3. *Ya.B. Losovyj, M. Klinke, En Cai, P.V. Galiy* et al. The electronic structure of surface chains in the layered semiconductor In_4Se_3(100) // Appl. Phys. Lett. 2008. Vol. 92. N 12. P. 122107-1–122107-3.
4. *Bercha D.M., Borets A.N., Stakhyra I.M., Tovstjuk K.D.* The band edge and the energy spectrum of In_2Se // Phys. Status Solidi. 1967. Vol. B21. N 2. P. 769–774.
5. *Bercha D.M., Kharkhalis L.Yu., Bercha A.I., Shnajder M.* Band Structure and Condenson States in In_4Se_3 Crystals // Phys. Stat. Sol. 1997. Vol. B203. P. 427–440.
6. *Sznajder M., Rushchanskii K.Z., Kharkhalis L.Yu.* et al. Similarities of the band structure of In_4Se_3 and InSe under pressure and peculiarities of the creation of the band gap // Phys. Stat. Sol. B. 2006. Vol. 243. N 3. P. 592–609.
7. *Galiy P.V., Nenchuk T.M., Dveriy O.R.* et al. Atomic force microscopy study of the cleavage surface of In_4Se_3 layered semiconductor crystal // Phys. E: Low-

dimensional Systems and Nanostructures. http://dx.doi.org/10.1016/j.physe.2008.09.011.

8. *Galiy P.V., Musyanovych A.V., Nenchuk T.M.* Electron Spectroscopy of the Interface Carbon Layer Formation on the Cleavage Surfaces of the Layered Semiconductor In_4Se_3 Crystals // J. Electron. Spectroscop. and Relat. Phenom. 2005. Vol. 142. N 2. P. 121–128.

НАНОРОЗМІРНІ ДОСЛІДЖЕННЯ (100) ПОВЕРХОНЬ КРИСТАЛІВ In_4Se_3 МЕТОДАМИ СТМ/СТС/АСМ

П. Галій[1], Т. Ненчук[1], О. Дверій[1], А. Цішевський[2], П. Мазур[2], С. Зубер[2]

[1]*Факультет електроніки Львівського національного університету ім. І.Франка, вул. Драгоманова, 50, 79005 Львів, Україна*
[2]*Інститут експериментальної фізики, Вроцлавський університет пл. М.Борна, 9, Вроцлав, 50-204, Республіка Польща*

Кристалографія та топографія (100) поверхонь сколювання кристалів шаруватих напівпровідників In_4Se_3 досліджена методами дифракції повільних електронів (ДПЕ), сканувальної тунельної та атомно-силової мікроскопії (СТМ, АСМ) у надвисокому вакуумі. Структура рефлексів ДПЕ, форма і характерні розміри в одержаних СТМ- та АСМ-профілях поверхонь сколювання відповідають структурі і параметрам ґратки, одержаних для кристалів In_4Se_3 орторомбічної структури методом дифракції Х-променів. Локальна густина поверхневих електронних станів і ширина забороненої зони для поверхонь (100) In_4Se_3, яка отримана методом сканувальної тунельної спектроскопії (СТС), свідчать про величину таку ж, як для “об’єму” кристалів, і про стабільність міжшарових поверхонь сколювання та перспективність використання сколів для формування поверхневих наноструктур, зокрема, нанодротів.

Ключові слова: низьковимірні структури, поверхні шаруватих напівпровідників, дифракція повільних електронів, сканувальна тунельна мікроскопія і спектроскопія, атомно-силова мікроскопія.

НАНОРАЗМЕРНЫЕ ИССЛЕДОВАНИЯ (100) ПОВЕРХНОСТЕЙ КРИСТАЛЛОВ In_4Se_3 МЕТОДАМИ СТМ/СТС/АСМ

П. Галий[1], Т. Ненчук[1], О. Дверий[1], А. Цишевский[2], П. Мазур[2], С. Зубер[2]

[1]*Факультет электроники Львовского национального университета имени Ивана Франко ул. Драгоманова, 50, 79005 Львов, Украина*
[2]*Институт экспериментальной физики, Вроцлавский университет пл. М.Борна, 9, Вроцлав, 50-204, Республика Польша*

Кристаллография и топография (100) поверхностей скалывания кристаллов слоистых полупроводников In_4Se_3 исследована методами дифракции медленных электронов (ДМЭ), сканирующей туннельной и атомной силовой микроскопии (СТМ, АСМ) в сверхвысоком вакууме. Структура рефлексов ДМЭ, форма и характерные размеры в полученных СТМ- и АСМ-профилях поверхностей скалывания отвечают структуре и параметрам решетки, полученных для кристаллов In_4Se_3 орторомбической структуры методом дифракции X-лучей. Локальная плотность поверхностных электронных состояний и ширина запрещенной зоны для поверхностей (100) In_4Se_3, которая получена методом сканирующей туннельной спектроскопии (СТС), свидетельствуют о величине такой же, как для “объема” кристаллов, и про стабильность межслойных поверхностей скалывания и перспективность использования сколов для формирования поверхностных наноструктур, в частности, нанопроводов.

Ключевые слова: низкоразмерные структуры, поверхности слоистых полупроводников, дифракция медленных электронов, сканирующая туннельная микроскопия, спектроскопия, атомно-силовая микроскопия.

Стаття надійшла до редколегії 12.11.2008
Прийнята до друку 25.03.2009