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Structural and energy changes at the cleavage surfaces of In_4Se_3 layered crystals under interface formation

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Structural and energy changes at the cleavage surfaces of In_4Se_3 layered crystals during interface formation have been studied by means of the ultraviolet photo-electron spectroscopy (UPS) and low-energy electron diffraction. The unintentionally doped In_4Se_3 crystal cleavages exposed to atmosphere of ultrahigh vacuum chamber residual gases, treated by Ar ion sputtering and UV illumination show the differences in UPS spectra which might be attributed to transformations of electron energy structure of the surface. The analysis of the interface formation at In_4Se_3 cleavages is of importance due to the ability to obtain reliable results of the In_4Se_3 band mapping, avoiding the effect of the cleavage surface instability under UV, ion treatment and exposure to ultrahigh vacuum, that is unusual for layered crystals.

Исследованы структурные и энергетические изменения на поверхностях скалывания слоистых кристаллов In_4Se_3 методами ультрафиолетовой фотоэлектронной спектроскопии (УФЭС) и дифракции медленных электронов. В УФЭС спектрах поверхностей скалывания чистых кристаллов In_4Se_3, экспонированных к атмосфере остаточных газов сверхвысоковакуумной камеры, обработанных ионами Ar и УФ облучением, обнаружены различия, которые могут быть связаны с изменениями в электронно-энергетической структуре поверхности. Рассмотрение формирования интерфейсов на сколах In_4Se_3 является важным с точки зрения получения достоверных результатов экспериментального исследования зонной структуры In_4Se_3 с исключением влияния нестабильности поверхностей скалывания под действием УФ, ионного облучения и экспозиции в сверхвысоком вакууме, которая не является характерной для слоистых кристаллов.

The layered crystal structures with weak interaction of van der Waals type between the layers and strong covalent-ionic interaction within the layer are recently studied giving new insights into the understanding of the properties of the low-dimensional (2D) structures and their potential technology applications [1–4]. Taking into account the crystal structure [5] with the surface rough in the atomic scale, In_4Se_3 might be promising material for formation of nanostructures (nanowires) on crystal cleavages. Our studies of In_4Se_3 [6, 7] give evidence that crystal cleavages obtained under ultrahigh vacuum (UHV) are characterized by high density of surface states and, consequently, by high adsorption activity, that is unusual for layered crystals [1–4, 6]. The model of CO adsorption on the UHV cleavages and formation of interfaces in air has been considered before [6, 7].

This study is aimed at the characterization of In_4Se_3 semiconductor crystal surface using the ultraviolet photoelectron

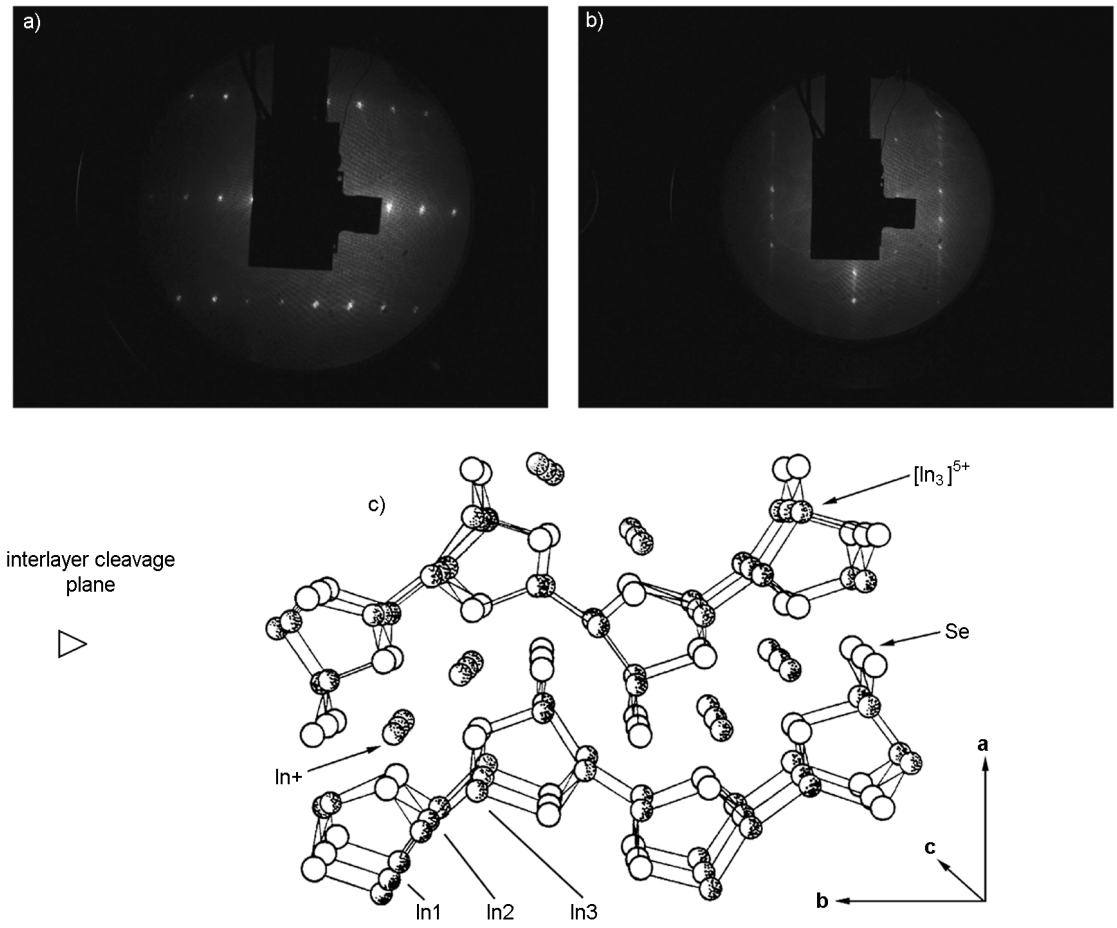

Fig. 1. LEED pattern (54 eV) of (100) In_4Se_3 cleavages: (*a*) just after the cleavage, (*b*) after exposure in UHV (during 12 hours); (c) interlayer cleavage (100) of In_4Se_3 structure fragment [5] (projection on (001) plane). Triangle shows the cleavage direction. $[In_3]^{5+}$ is polycation of indium (In1, In2, In3); In^+, cation of indium (In4). The lattice constants: **a** = 15.296(1) Å; **b** = 12.308(1) Å; **c** = 4.0806(5) Å; space group P_{nnm} [6]. The cleavage plane (100) is normal to the axis of crystal growth **a**.

spectroscopy (UPS). The most of the emitted photoelectrons originate from the first few atomic layers of the crystal and, therefore, the formation of the interfaces on In_4Se_3 cleavages influences significantly its UPS spectra. The *in situ* analysis of the interface formation at the cleavages just after the cleaving, after exposure to the residual gas atmosphere and after other treatments such as ion sputtering and light illumination is the first step to In_4Se_3 experimental band mapping, to avoid the effects of the cleavage high reactivity unusual for the layered crystals. The UPS studies were carried out using synchrotron radiation dispersed by a 3 m toroidal grating monochromator (3m TGM beamline) described elsewhere [8, 9]. The end station consisted of an UHV system with turbo molecular pumping operating at a pressure of $1.5 \cdot 10^{-10}$ Torr. The UHV residual gas atmosphere consisted mainly of CO, H_2O, H_2 and also negligible amounts of hydrocarbons at partial pressures lower than 10^{-12} Torr. The photon energies in the 18–110 eV range were applied. The combined resolution of the electron energy analyzer and monochromator is 120–150 meV for 50–120 eV kinetic photon energies, but a higher resolution (about 80 meV) is obtained at 15–40 eV photon energies. All binding energies were referenced to the Fermi level, as determined using pure gold. The UPS was performed in normal emission mode with application of *s*+*p*- and *p*-polarization of incident light. The low-energy electron diffraction (LEED) patterns have been studied just after the cleavage and after exposure to UHV residual gas atmosphere of the end station. The In_4Se_3 layered crystals ($3 \times 6 \times 4$ mm^3 samples with a special

shape for cleavage in UHV) have been grown by Czochralski method. In both UPS and LEED studies, the samples were cleaved *in situ* at room temperature in the side chamber using a low profile stainless steel microtome blade. The crystal structure of unintentionally doped In_4Se_3 has been considered in [5] and is presented in Fig. 1(c). UPS was used to characterize the evolution of the occupied valence band (VB) states and In 4d and Se 3d core levels during the formation of carbon/In_4Se_3 interface. The UPS studies were performed with In_4Se_3 (100) surfaces just after the cleavage in UHV and its further exposure *in situ*. Moreover, the UPS spectra of "as-inserted" cleavages, long term exposed to laboratory atmosphere, were inspected. The influence of surface treatment by illumination with 3 m TGM zero order light (undispersed) and Ar^+ ion sputtering on the UPS spectra was considered.

The perfect crystal structure of the *in situ* cleavage through the macroscopic sample area is confirmed by the LEED pattern, Fig. 1. The crystals were cleaved along two perpendicular directions **b** or **c** in the layer plane (Fig. 1a or 1b). The LEED pattern of the sample shows the orthorhombic symmetry of the crystal while the distances between sites in different directions evidence a high value of **b**/**c** space lattice parameter ratio that is characteristic for this crystal [10]. The cleavage surfaces do not appear to exhibit any lateral reconstruction and are stable in UHV. The exposure of cleavages *in situ* and, consequently, formation of coating on the surface cause only an insignificant LEED pattern blurring (Fig. 1b).

Fig. 2 shows a wide scan ($E_{h\nu}$ = 110 eV) of In_4Se_3 crystal as inserted after exposition *ex situ* (old cleavage) and after the cleavage in UHV. Fig. 2, curve *4* evidences the existence of some new phase on the old cleavages (intense peak at 8–8.5 eV binding energy), moreover, heating up to 330 K and zero order light treatment modify the UPS spectrum shape with increase of this peak intensity and its transformation into two peaks at 7.0–7.2 and 10–11 eV binding energies. Simultaneously, the surface cleaning effect is observed while considering the spectrum in the binding energy ranges at In 4d and much more noticeable at Se 3d core levels. Nevertheless, the most pronounced changes occur in the binding energy range of In_4Se_3 valence band (VB) (cf. Fig. 2, curves *1*, *5*, *6*) for UHV cleavages studied just after the cleavage and after exposure

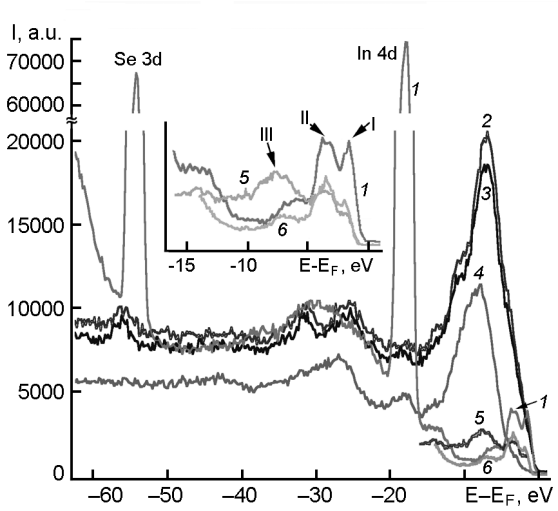

Fig. 2. The wide scan and valence band (VB) UPS spectra (normal emission) of In_4Se_3 ($h\nu$ = 110 eV, *s*+*p* polarization): *1*, just after the cleavage in UHV; *2*, "old" cleavage after zero order light cleaning for 15 min; *3*, the same "old" cleavage as for *2* after further *in situ* exposure for 15 h; *4*, uncleaned "old" cleavage; *5*, UHV cleavage VB after exposure *in situ* for 35 h (19 L); *6*, UHV cleavage VB after exposure *in situ* for 26 h (14 L). Inset: the three distinct features I, II, III in the UPS spectra.

in situ for ~14–19 Langmuir units (L). The inset in Fig. 2 displays the three characteristic structure features observed in UPS spectra of In_4Se_3, especially, the features I and II occur for atomically clean surfaces. The feature III increases after *in situ* exposure of UHV cleavage. The In_4Se_3 energy gap values published by various authors vary between 0.62 and 0.67 eV at 300 K. The band structure calculations have shown that In_4Se_3 is direct gap material with complex VB structure [11, 12]. Consequently, the two distinct groups of peaks denoted as I and II at lower binding energies may be assumed to represent In_4Se_3 VB and the feature III correlates with new bindings that occur at the In_4Se_3 surface after UHV exposure.

As to the interface formation, the studies of the possible dispersion and intensity redistribution of these features were conducted in the wide range of incident photons' energies and expositions. Fig. 3 show the VB UPS spectra of UHV obtained and exposed In_4Se_3 surfaces ($h\nu$ = 18, 25 and 110 eV; *s*+*p* polarization) with features I and II. Their complex structure is well resolved. Fig. 3b, curve *4* shows drastic changes in the UPS spectrum after the sur-

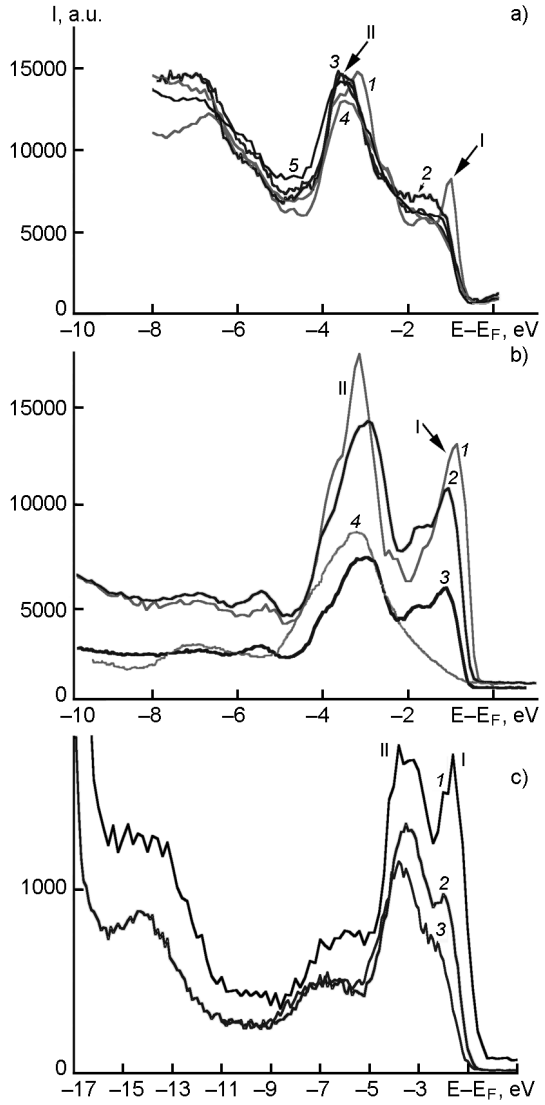

Fig. 3. UPS data of the VB (normal emission) from In_4Se_3 UHV cleavage surfaces after different exposures in UHV. (a) ($h\nu$ = 18 eV, s+p polarization): *1*, 3.5 h; *2*, 7 h; *3*, 22 h; *4*, 56 h; *5*, 245 h; (*b*) ($h\nu$ = 25 eV, s+p polarization): *1*, 15 min; *2*, 32 h; *3*, 73 h; *4*, Ar^+ ion sputtered for 10 min (E = 1.6 keV, I = 10 μA, $P_{Ar} = 5 \cdot 10^{-5}$ Torr); (c) ($h\nu$ = 110 eV, s+p polarization): *1*, 15 min; *2*, 26 h; *3*, 194 h.

face cleaning by Ar^+ ion sputtering, with disappearance of feature I. The Ar^+ sputtering yield of Se atoms is approximately 1.1 times higher than for In ones. Thus, as a result of ion sputtering, the cleavage surface is enriched in In atoms. Consequently, the VB energy spectrum is changed.

The detailed examination of the UPS spectra in Fig. 4 obtained from the surfaces after a long term exposure *in situ*, evi-

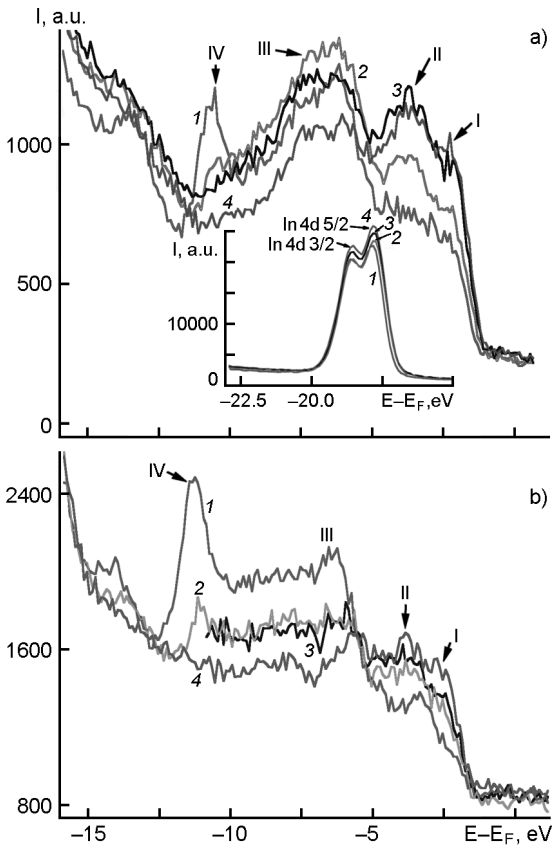

Fig. 4. UPS spectra (normal emission) of VB from different areas of In_4Se_3 surface cleaned by synchrotron zero order irradiation (preliminary the surfaces have been exposed for ≈196 h–215 h (106 L–116 L) in UHV). **(a)** ($h\nu$ = 62 eV, p-polarization): *1*, initial spectrum; *2*, *3*, *4*, different cleaning durations: ≈10 s, ≈20 s, ≈2–3 min, respectively. Inset; spectra of In 4d core level corresponding to above VB spectra; **(b)** ($h\nu$ = 40 eV, p-polarization): *1*, upper part of the sample; *2*, middle part; *3*, middle part cleaned by synchrotron zero order irradiation; *4*, bottom part (the contamination drops in the direction from upper part to bottom).

dences some reversible temporary changes in peak intensities and binding energies. In such cases, it is difficult to establish the peak intensity and binding energy dependences on the exposure conditions, that might be caused by complex influence of irradiation on transformations in the interface layer. The most evident effect of surface "cleaning" might be observed under zero order light irradiation. In order to increase light intensity during such treatment, the samples are irradiated at zero order, thus, photons from both VUV and soft X-ray ranges (15–350 eV) reach the

sample surface. Moreover, the conclusion that the features I and II are attributed to electron states of Se and In, respectively, becomes more convincing after the inspection of the changes in the UPS spectra of the surfaces after prolonged exposures *in situ* and influence of zero order light cleaning. The intensities of both I and II features for such spectra (Fig. 4) are relatively small and their structure seems to be not resolved well, while the feature III is intense and additionally the feature IV appears. The spectra in Fig. 4 are obtained with *p*-polarized light, that provides a higher surface sensitivity. The spectra transformations at increasing zero light treatment are the same for different energies of exciting photons (40, 62 eV) and, besides, shows the inverse character to the interface formation kinetics (Figs. 2, 3). The inset in Fig. 4a shows the UPS data of In 4d core level, where the doublet (In 4d 5/2 and 4d 3/2 peaks) is resolved. The doublet intensity changes like those of the I, II features and in inverse relation to the feature III intensity and shows a pronounced dependence on the zero order light treatment. Its intensity rises unambiguously with increasing zero order light illumination time of the surface. Moreover, the consideration of Se 3d and In 4d core levels in Fig. 2, curves *2–4*, reveals a higher cleaning degree of the surface Se atoms than In ones, taking also in account differences in kinetic energies of the corresponding photoelectrons.

Thus, the experimental UPS spectra of In_4Se_3 cleavages reveal several distinct structures. As the coating increases, the various features indicated as I, II, III and IV become more evident or disappear in the UPS spectra, additionally, the intensity difference between the features I and II increases with exposure. There is no doubt a decreasing in the intensity of feature IV (at 10–11 eV binding energies) in Fig. 4, with its disappearance after zero order light cleaning, probably connected with C 2p. The feature IV is clearly observed only for *p*-polarized light on surfaces long term exposed *in situ*. However, curves *4*, *3*, *2* in Fig. 2 show transformation of the broad peak at ≈8–8.5 eV binding energies characteristic for "untreated" old cleavages into two peaks at 7.0–7.2 and 10–11 eV binding energies after zero order light cleaning. Such peak energies are characteristic for features III and IV, respectively, appearing on cleavages long exposed *in situ*. Thus, a similarity in the interface formation could be concluded for the In_4Se_3 cleavages obtained *ex situ* and obtained *in situ* with subsequent long term exposure *in situ*. The feature III intensity increases with exposure in UHV, while intensity of In 4d and Se 3d core peaks decreases. On the whole, the changes observed in the core level intensities are small. The changes are more evident in the VB of In_4Se_3, where the presence of carbon has caused redistribution of the bonding units — Se 4p and In 5p contributions to the VB and, therefore, changes in the I and II feature intensities. Thus, the intensity decrease in the VB features I, II and increase of III, IV ones for the cleavages exposed *in situ* results from the interface formation on the surface.

Besides, we have to take into consideration the results of Auger electron spectroscopy coating kinetics during the interface formation in UHV for In_4Se_3 cleavages [6]. The UPS spectra presented in Fig. 3 are obtained under exposure *in situ* up to ≈130 L, commensurable to that used at AES kinetics studies [6, 13], that is sufficient for the prior Se and next In surface atoms coating with CO molecules. The intensity change in I and II features is not uniform. The feature I one changes its intensity more than II under exposure *in situ*. Thus, UPS results correlate well with our previous AES results [6], where Se atoms on the surface of unintentionally doped In_4Se_3 are the sites of primary CO adsorption *in situ* and carbon interface formation on the In_4Se_3 surface. The AES data on cleavages obtained *ex situ* just before introducing into UHV chamber (fresh) or long term exposed (>24 h) *ex situ* (old) indicated the carbon coating formation with small amounts of oxygen for old cleavages. Besides, the XPS data for Se 3d and C 1s core levels on In_4Se_3 fresh cleavages indicate that bindings formed by carbon are attributed to C–Se and C–C electron interactions [14]. The Se 3d spectral structure changes its shape to almost complete disappearance of the spin-orbit split doublet ($3d_{5/2}$ and $3d_{3/2}$) signals, especially, for old *ex situ* cleavages. While the XPS consideration of In 3d core level shows the formation of metallic and In_2O_3 oxidized phase for fresh and, especially, old *ex situ* cleavages.

Thus, in spite of the crystal and electron structure of the layer, the In_4Se_3 cleavages are unstable and not inert to gases adsorption, even in UHV conditions. The presence of the interface layers formed on the In_4Se_3 surfaces obtained by cleavage both in the

air and in UHV influences considerably the UPS spectra and the LEED patterns. As to UHV cleavages, the largest changes in UPS spectra occur when the cleavage has been exposed to atmosphere of UHV residual gases, though the smaller changes are induced by further VUV irradiation during spectra recording and zero order light treatment. Thus, one has also to distinguish whether the area now under study on the cleavage surface has been irradiated previously or not. On the whole, it might be assumed that the most reliable results of the UPS spectra recording for band mapping of the In_4Se_3 crystal could be obtained up to ≈2 L exposition *in situ*, but there is enough clean surface even up to 12–13 L exposition *in situ*. The UPS spectra of Ar^+ ion sputtered In_4Se_3 surfaces are rather distinct from those for *in situ* cleavages, obviously due to the differential sputtering effects and, consequently, are not suitable for band mapping. The UPS studies of the interfaces formed on *ex situ* cleavages and *in situ* ones after prolonged exposures (several hundreds of Langmuir units) in the atmosphere of residual UHV gases evidence a similarity in the interface formation on the In_4Se_3 surfaces with formation of new carbon containing phase.

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Структурні і енергетичні зміни на поверхнях сколювання шаруватих кристалів In_4Se_3 під час формування інтерфейсів

П.В.Галій, Т.М.Ненчук, Я.Б.Лозовий, Я.М.Фіяла

Досліджено структурні і енергетичні зміни на поверхнях сколювання шаруватих кристалів In_4Se_3 методами ультрафіолетової фото-електронної спектроскопії (УФЕС) і дифракції повільних електронів. Проаналізовано відмінності в УФЕС спектрах поверхонь сколювання чистих кристалів In_4Se_3, експонованих у атмосфері залишкових газів надвисоковакуумної камери, підданих обробці іонами Ar і УФ опроміненням, які можуть бути пов'язані із змінами електронно-енергетичної структури поверхні. Проведені дослідження формування інтерфейсів на сколах In_4Se_3 є важливими з огляду на можливості отримання достовірних результатів експериментального дослідження зонної структури In_4Se_3, зважаючи на нестабільність поверхонь сколів під дією УФ, іонного опромінення і експозиції у надвисокому вакуумі, яка не є характерною для шаруватих кристалів.