

X-ray photoelectron spectroscopy of the interface phase on cleavage surfaces of the layered semiconductor In_4Se_3 crystals

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The results of X-ray photoelectron spectroscopy of the phase interface formation on the cleavage surfaces of layered semiconductor In_4Se_3 , $\text{In}_4\text{Se}_3(\text{Cu})$ crystals are presented. The peculiarities of the process in the high-vacuum chamber atmosphere have been studied using the Auger electron spectroscopy. The carbon and oxygen interface coatings are formed due to interaction of the air with atomically clean cleavage surfaces of the crystals pure In_4Se_3 and $\text{In}_4\text{Se}_3(\text{Cu})$ crystals.

Представлены результаты исследования формирования междуфазных границ на поверхностях скалывания кристаллов слоистых полупроводников In_4Se_3 , $\text{In}_4\text{Se}_3(\text{Cu})$, полученные методом рентгеновской фотоэлектронной спектроскопии (РФЭС). Особенности этого процесса в атмосфере остаточных газов сверхвысоковакуумной камеры исследованы методом оже-электронной спектроскопии (ОЭС). Углерод-кислородные интерфейсные покрытия на междуслойных поверхностях скалывания формируются вследствие взаимодействия воздуха с атомарно чистыми поверхностями скалывания кристаллов.

The layered semiconductor crystals In_4Se_3 are characterized by a weak van der Waals type interaction between the layers (thus making it possible to obtain high-quality cleavage surfaces) and strong covalent-ionic one inside the layers. The quasi-two-dimensionality of this material with no dangling electron bonds on cleavages [1, 2] results in some peculiarities of adsorption, in particular, a significant inertness or selectivity depending on the specific adsorbate-substrate system. The adsorption model of CO at the ultrahigh vacuum cleavage (100) surfaces of In_4Se_3 with its dissociation and carbon chemisorption has been considered in [3]. Thus, taking into account results of our previous studies [4], it is evident that In_4Se_3 is a prospective material as a CO gas adsorbent or possible CO gas

sensor and might be used in functional electronics [5].

In this study, we focus on the quantitative analysis of interface formation at the cleavage surfaces of In_4Se_3 layered semiconductor crystal under air exposure at room temperature and peculiarities of the interface layer formation. This paper reports X-ray photoelectron spectroscopy (XPS) study results of In_4Se_3 pure and copper-intercalated crystal cleavage surfaces. The presented XPS investigation results of the layered semiconductor In_4Se_3 crystals are interesting also for complete XPS database [6], since the XPS spectral data for this crystal are absent and their publication will be benefit for other members of the materials and surface science community.

The layered crystal structure provides obtaining of excellent cleavage surfaces

with a relative small number of defects that are at the same time the interlayer (100) planes of In_4Se_3 crystal structure. The crystals were grown by Czochralski method at one of our laboratories. The further heat treatment of In_4Se_3 crystal containing copper impurity ($\text{In}_4\text{Se}_3(\text{Cu})$) in evacuated quartz ampoules during 30 hours at 540 K results in Cu intercalation. The XPS quantitative analysis shows that the average surface concentration of Cu is 0.22 to 0.25 at.%. According to X-ray structural analysis, the presence of such Cu concentrations allows to obtain $\text{In}_4\text{Se}_3(\text{Cu})$ crystals with well-layered structure. Both pure and copper-intercalated In_4Se_3 crystals were investigated.

The crystals interlayer cleavage surfaces (see Fig. 1) were obtained in air. The crystal structure of pure In_4Se_3 has been considered before [1] and later in [2]. The lack of reconstruction of the surface layer is typical of layered crystals, what has been testified, in particular, by the results of STM studies [7–9]. The method of pure elemental standards [10, 11] was used to the quantitative XPS of the interface layer formation at the cleavage surfaces of the layered In_4Se_3 crystals.

The XPS spectra were obtained for interface formation at the cleavage surfaces of air-exposed In_4Se_3 , $\text{In}_4\text{Se}_3(\text{Cu})$ layered semiconductor crystals. The cleavages obtained in air were then brought into contact with N_2 , O_2 , CO_2 , CO , H_2O , CH_x atmospheres. Those exposed for approximately 2–15 min are called "fresh" cleavages (FRC) and those exposed for a longer time (more than 24 h) are called "old" cleavages (OLC). The XPS studies were carried out using an AXIS ULTRA (Kratos Analytical, England) equipment, employing monochromatic aluminum K_α X-rays ($h\nu = 1486.6$ eV) and full width of half maximum (FWHM) of 0.3 eV at an electron take-off angle of 90° . The spectrometer was calibrated using the $\text{Ag } 3d_{5/2}$ line at 368.2 eV with FWHM at 1.7 eV. The energy resolution of the analyzer was 1.5 %. The data were collected using a concentric hemispherical analyzer (CHA) fitted with a Channeltron detector and the Charged Coupled Device (CCD) camera. The spectral data from the output of the rate meter were stored in an IBM PC. The repeated scan and data summation were used in order to increase the signal-to-noise ratio. In this way, the data were obtained enabling the data smoothing, background correction, and determination of binding energies at peak positions and peak

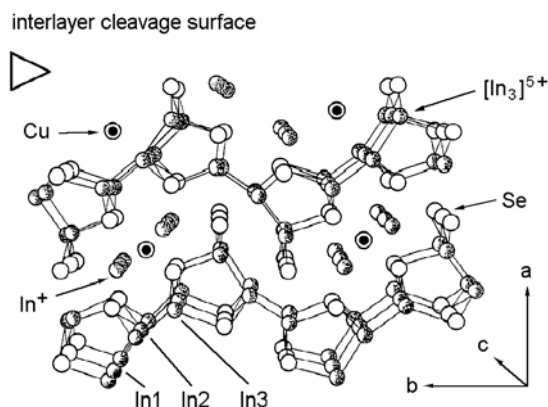


Fig. 1. Interlayer cleavage plane (100) of In_4Se_3 crystal structure fragment according to [2] (projection of (001) plane). Triangle upper left shows the cleavage direction, $[\text{In}_3]^{5+}$ is polycation of indium (In1, In2, In3); In^+ , cation of indium (In4) and intercalated copper impurity of Cu in interlayer space. The lattice spaces of crystal structure: $a = 15.296(1)$ Å; $b = 12.308(1)$ Å; $c = 4.0806(5)$ Å; space group P_{nm} [2].

areas. The peak areas can be used to determine the composition of the interface layer at the surface. The shape of each peak and the binding energy can be slightly altered depending on the emitting atom chemical state. Hence, XPS can provide information about chemical bonding as well. The pressure of residual gas atmosphere in the UHV spectrometer chamber was typically $1.3 \cdot 10^{-7}$ Pa during the spectra recording. The samples were fixed on a metallic stub with conducting tape. A wide scanning (0–1100 eV) was recorded for each sample. The analyzer was operated at the pass energy of 160 eV (wide-scan) and 20 eV and an expanded binding energy scale (Se $3d_{5/2}$, C 1s, In $3d_{5/2}$, O 1s, Cu $2p_{3/2}$ regions).

The presence of carbon at the "fresh" and "old" cleavage surfaces was confirmed by XPS analysis. Fig. 2(a,b) show typical XPS wide-scan spectra (0–1100 eV) for the interface formation on the "fresh" (FRC) and "old" cleavages (OLC) surfaces of In_4Se_3 layered crystals where the most intense and other repeated peaks are identified. The presence of carbon at the FRC and OLC surfaces may result not only from hydrocarbon contamination [3, 4, 13] but arises from the presence of other adsorbed gases (see Fig. 3(a,b)).

The most intense XPS lines, viz. Se $3d$, In $3d_{5/2}$, C 1s, O 1s and the sharpest Auger lines, viz. Se LMM, In MNN and O KLL, were recorded in an expanded binding en-

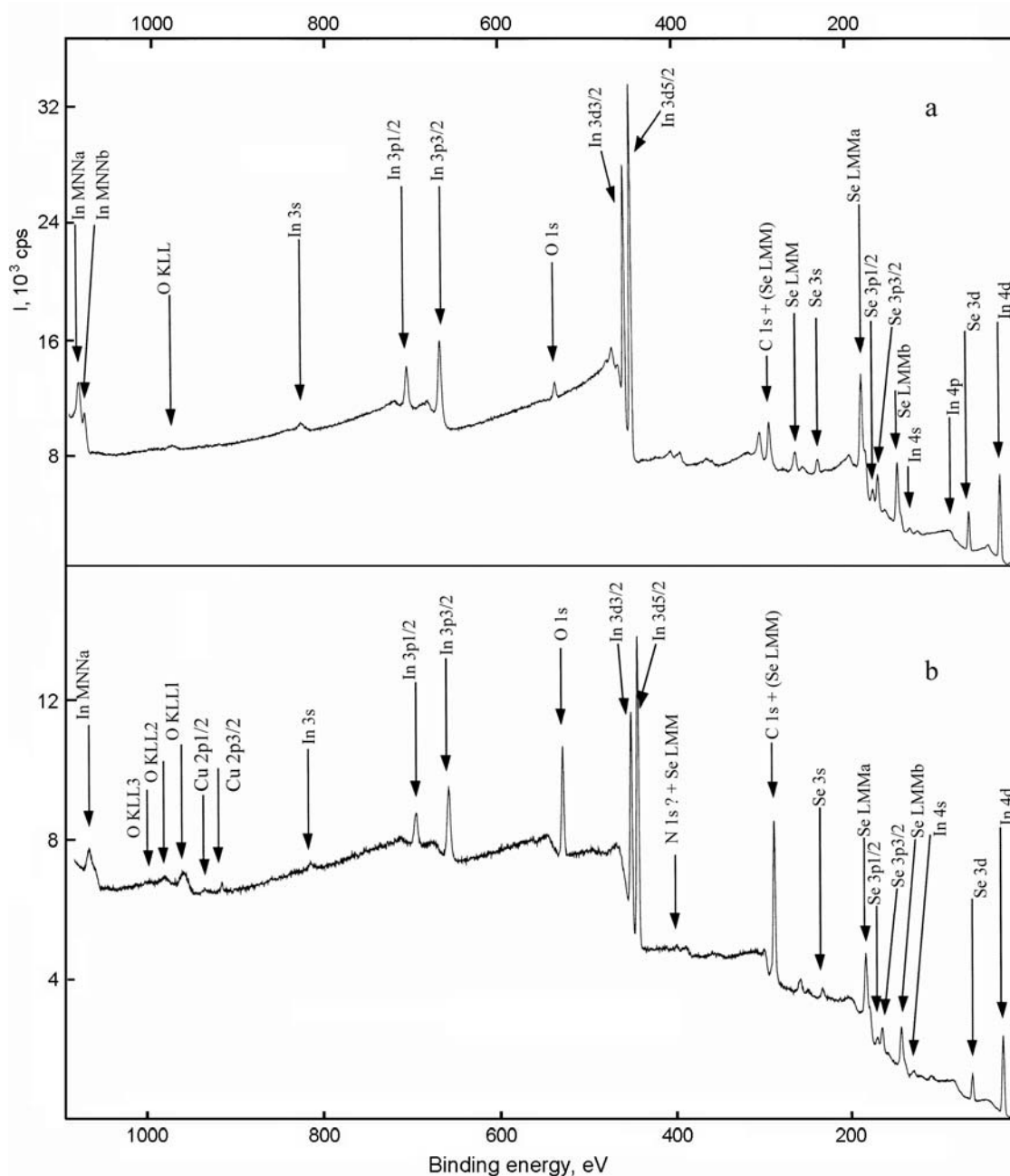


Fig. 2. Wide-scan XPS spectra of the interface formation at the cleavage surfaces of pure and copper-intercalated In_4Se_3 crystals: (a), "fresh" cleavage surfaces (FRC) of In_4Se_3 ; (b), "old" cleavage surfaces (OLC) of the intercalated $\text{In}_4\text{Se}_3(\text{Cu})$.

ergy scale to calculate the atomic concentrations and to estimate the adsorbate \rightarrow substrate charge transfer Δq [3]. The control of the sample charging takes place and this was corrected by taking the 1s line at 284.5 eV carbon as a reference in all cases. The exact peak positions of these intense lines were subsequently determined from the corresponding profiles recorded on an

expanded binding energy scale and are shown for Se 3d, In 3d_{5/2} and Cu 2p_{3/2} in Fig. 4, and for C 1s, in Fig. 5. In each case, Gaussian line shape analysis was done for the XPS expanded profiles after making the background correction using Shirley method [12] to determine the exact peak position and peak area. The chemical shifts ΔE_C could be calculated from the binding energy

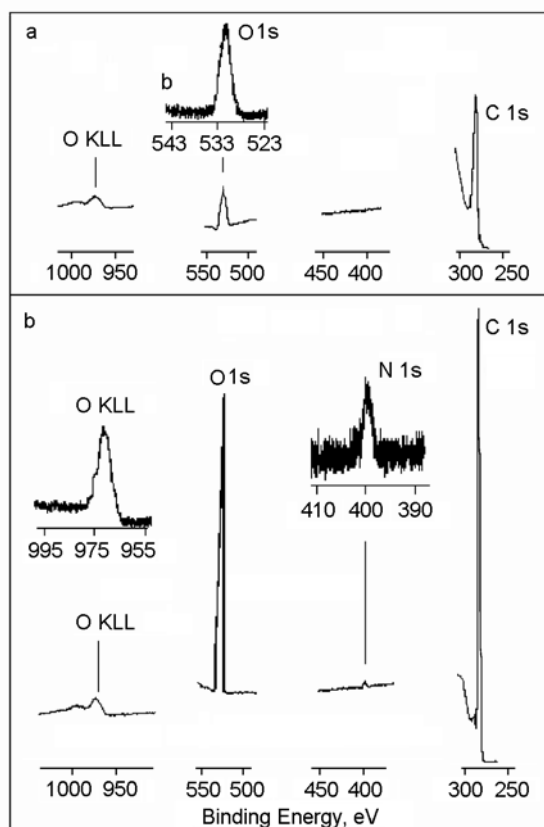


Fig. 3. Fragments of the some adsorbate peaks in the wide-scan XPS spectra of the interface formation at the cleavage surfaces of In_4Se_3 crystals: (a), "fresh" cleavage surfaces (FRC); (b), old cleavage surfaces (OLC) with negligible background correction.

values for the XPS lines of Se, In, C and O, corrected with reference to vacuum level.

The C 1s peak at 284.39 eV and O 1s one at 530.99 eV (Fig. 2(b), Fig. 3) contribute mainly to the XPS spectrum of the interface for the OLC In_4Se_3 surface, but there are also intense signals at 443.99 ($3d_{5/2}$) eV and 408.0 ($M_4N_{4,5}N_{4s}$) eV corresponding to the In $3d_{5/2}$ core level and In $M_4N_{4,5}N_{4s}$ -Auger transition and the signal at 53.69 eV corresponding to the Se ($3d_{5/2} + 3d_{3/2}$) levels [10]. XPS wide-scan of the OLCs surface interface indicates the missing of nitrogen N 1s peak at 400.0 eV (Fig. 3(b)), thus confirming the presence of only slightly physically adsorbed nitrogen on the OLCs surface exposed to air. The nitrogen that is slightly adsorbed in air becomes desorbed from the surface in UHV conditions. In the XPS wide-scan spectrum of the FRC surface interface (Fig. 3(a)), nitrogen N 1s peak is absent, too. A strong decrease of the (O/C) and (N/C) peak area ratios is observed for

FRC as compared to the same for OLC. This indicates that in UHV XPS-chamber, the adsorbed nitrogen (N_2) is absent and carbon monoxide is the main adsorbate at the In_4Se_3 surface, and it forms In_4Se_3 -C interface during CO adsorption with its dissociation and carbon chemisorption, as it was found by mass-spectroscopy and Auger electron spectroscopy (AES) studies of In_4Se_3 UHV cleavages *in situ* [3, 4, 13].

In the expanded-scan XPS spectra for FRCs surfaces, the binding energy peak of indium atoms In $3d_{5/2}$ at 444.0 eV indicates that indium atoms form the metallic binding (for metallic indium, In $3d_{5/2}$ 443.84–443.9 eV [10]) slightly shifting to In $3d_{5/2}$ 443.99 eV for the OLC surfaces (Fig. 4(a,b)). The formation of In–In metallic binding and metallic phase on the free cleavage surfaces of In_4Se_3 is possible due to the slight $\text{In}^+(\text{In}4)$ cationic bindings with the layer packets (Fig. 1). The mean In–In binding length of is 2.77 Å for the three In1, In2, In3 atoms, that is shorter than one for metallic indium (3.24–3.36 Å). Thus, these structures contain a polycation consisting of three atoms $[\text{In}_3]^{5+}$ and bindings for these structures are ionic-covalent, but non-metallic ones [1, 2]. The Se atoms are in sp^3 -hybridized state and each is bonded with three indium atoms and the selenium atoms are in the double-ionized state Se^{2-} [1, 2].

Fig. 4(b) with XPS spectra expanded-scan for the OLC surfaces shows the formation of metallic and In_2O_3 oxidized phase for which the binding energy peak of the In $3d_{5/2}$ is observed at 444.4 eV [10]. The obtained binding energy Se $3d_{5/2}$ peaks for FRC at 54.3 eV and for OLC Se ($3d_{5/2} + 3d_{3/2}$) at 53.69 eV surfaces of In_4Se_3 (Fig. 4(a,b)) also indicate the oxygen interaction with indium atoms and formation of oxidized In_2O_3 [10] and the selenium atom interaction with carbon during CO adsorption with its decomposition resulting in oxygen desorption and carbon 5σ -binding with the surface of layered crystals (Se–C bindings [3]). It is well known that under SeO_2 oxide formation, the binding energy peak Se $3d_{5/2}$ is observed at 58.8 eV [10], while it is absent for FRC and OLC surfaces of In_4Se_3 . At the same time, the In–O binding formation could be observed clearly in the expanded-scan XPS spectra, and Se–C binding formation also takes places as it is seen from XPS (Fig. 4(a,b), Fig. 5(a,b)) and our AES results [3, 13]. It is to note that for OLC, shifts in Cu $2p_{3/2}$ peak position from

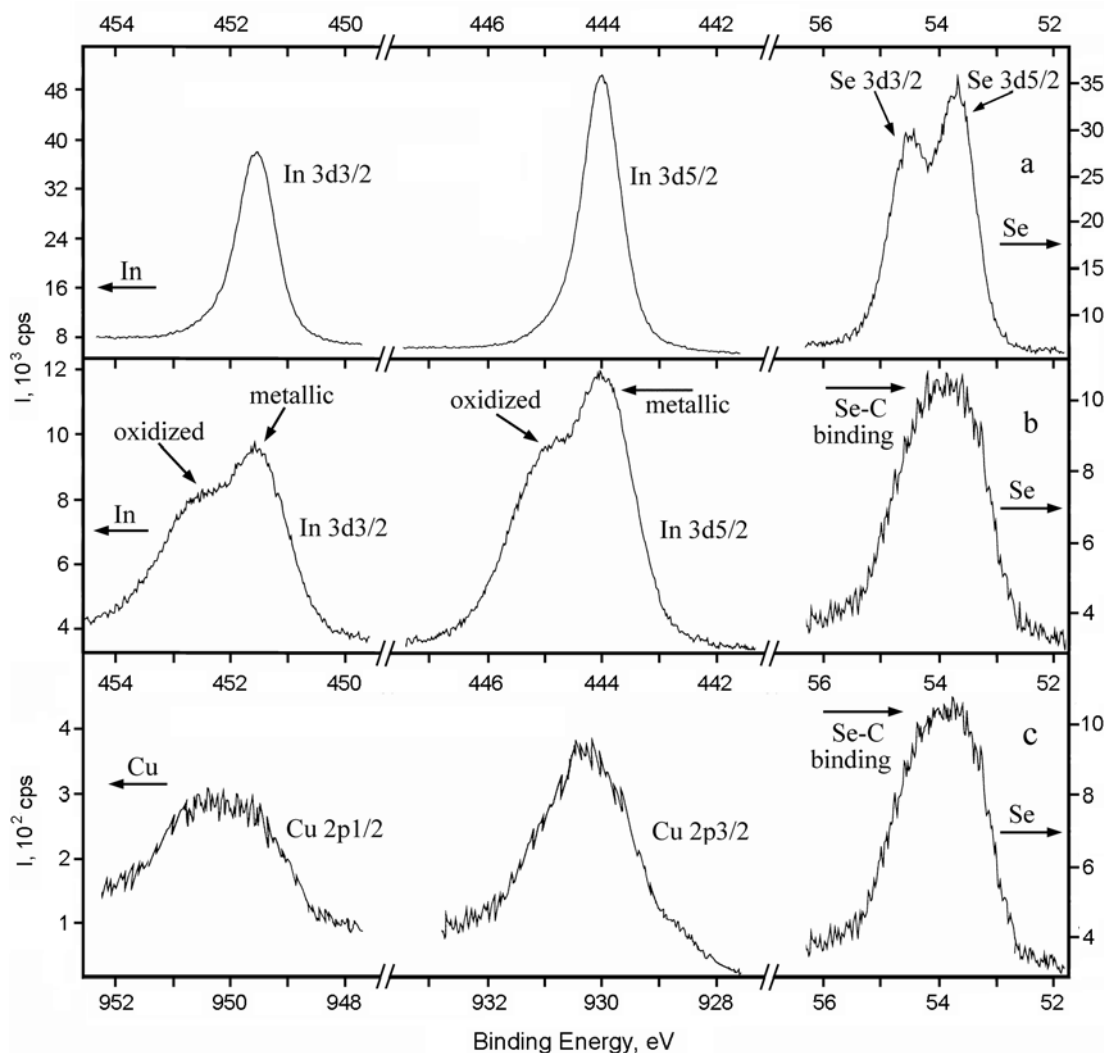


Fig. 4. Expanded-scan XPS spectra of the matrix components ($\text{Se } 3d_{5/2}$; $\text{Se } 3d_{3/2}$; and $\text{In } 3d_{5/2}$; $\text{In } 3d_{3/2}$) for the cleavage surfaces of In_4Se_3 (a, b) crystals: (a), "fresh" cleavage surfaces (FRC); (b), "old" cleavage surfaces (OLC); (c), OLC of intercalated $\text{In}_4\text{Se}_3(\text{Cu})$ ($\text{Se } 3d$; $\text{Cu } 2p_{3/2}$ and $\text{Cu } 2p_{1/2}$).

931.8 eV for metallic Cu–Cu binding to $\text{Cu } 2p_{3/2}$ (930.59 eV), $\text{In } 3d_{5/2}$ (443.99 eV) and $\text{Se } 3d$ (53.71 eV) confirm the possibility of Cu–In–Se bindings. The $\text{Cu } 2p_{3/2}$, $\text{In } 3d_{5/2}$, $\text{Se } 3d$ binding energies are close to those for CuInSe_2 [10]. The presence of non-simple interaction in the In_4Se_3 –C interfaces at the OLC and FRC surfaces can be confirmed also by a closer inspection of the C 1s core level of XPS spectra shown in Fig. 5, the when analyzer was operated with the pass energy of 20 eV (precise-scan) in C 1s region. The Shirley background subtraction in the least squares fittings is used for inspection of the C 1s core level [12]. The peak positions and widths are determined from least squares fitting using the standard for this equipment software. The peak shapes for

all peaks are fixed to a mix of 80 % Gaussian — 20 % Lorentzian with no asymmetry.

The decomposition for C 1s carbon peak is obtained using the existing database and software for organic compounds. The decomposed C 1s (284.7 eV) XPS peak for FRCs of In_4Se_3 –C,O surface interface (Fig. 5(a)) shows the presence of at least three types of carbon. Those could be attributed as C–Se (284.7 eV); C–O (286.0 eV) and C=O (287.0 eV) interactions (bonds). The decomposed carbon C 1s peak for the OLC of In_4Se_3 surface interface (Fig. 5(b)) shows peaks at 284.39 eV attributed to C–Se; C–C interaction in the "graphite phase" or C–C/C–H (285.0 eV); C–O; C=O, and possibly C–N (285.7 eV). The last one is confirmed by the presence of N 1s (400.0 eV) peak in the spectra (Fig. 3(b)) and its negligible amount

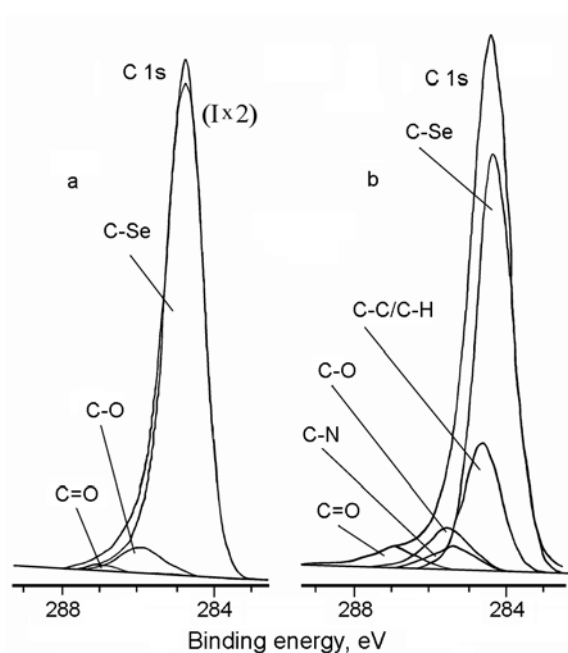


Fig. 5. Expanded-scan XPS spectra of the decomposed C 1s peak with background correction for $\text{In}_4\text{Se}_3\text{-C}_x\text{O}_y$ interface system: (a), "fresh" cleavage surfaces (FRC); (b), old cleavage surfaces (OLC). The peak intensities are multiplied by two for the expanded-scan XPS spectra of the FRC surfaces.

at the OLC of In_4Se_3 surface. It is to note that C=O or C-N type bindings obtained from C 1s peak decomposition are not necessarily implemented in the adsorbed coatings at for-

mation of the $\text{In}_4\text{Se}_3\text{-C}_x\text{O}_y$ interface layer. C=O and C-N bindings (see Fig. 5) are result only from the C 1s peak decomposition using the software for organic compounds. At the same time, In-O and Se-C bindings exist really in the $\text{In}_4\text{Se}_3\text{-C}_x\text{O}_y$ interface layer with the formation of "graphite" phase (C-C interactions) under carbon coverage degree $\theta \geq 1$ [3].

The surface compositions for the series of the "fresh" and "old" cleavages of In_4Se_3 interface that have been calculated from the experimental XPS results are presented in Table 1 together with the XPS peak position. The binding energy values of Se $3d_{5/2}$, In $3d_{5/2}$, Cu $2p_{3/2}$, C 1s, and O 1s are in good agreement to those reported before [10]. It must be pointed out that the surfaces of analyzed samples are not smooth at the atomic scale, but rough ones (Fig. 1), and moreover, the samples were exposed to air. Therefore, the data obtained by XPS measurements could not express the exact absolute surface atomic concentrations and are considered as relative values.

The atomic concentrations C_i of the elements in the thin interface layer ($d \leq 15\text{-}25 \text{ \AA}$) were calculated from the peak areas for different interfaces using the formula [10]

$$C_i = \frac{I_i/S_i}{\sum_i I_i/S_i}, \quad (1)$$

where I_i is the area under the peak and S_i is the atomic sensitivity factor of the emit-

Table 1. XPS results of the interfaces formed on the FRC and OLC surfaces of the In_4Se_3 , $\text{In}_4\text{Se}_3(\text{Cu})$ crystal

	Element peak	Binding energy, eV	FWHM, eV	Raw area, (cps)	Sensitivity factor, a.u.	Atomic conc., %
FRC In_4Se_3 crystal surfaces	O 1s	531.60	3.468	42723.0	0.780	12.53
	In $3d_{5/2}$	444.00	2.562	677694.0	4.359	36.44
	C 1s	284.70	2.583	42927.5	0.278	34.57
	Se $3d_{5/2}$	54.30	2.655	72862.8	0.853	16.46
OLC In_4Se_3 crystal surfaces	O 1s	530.99	2.963	102233.0	0.780	18.32
	In $3d_{5/2}$	443.99	2.881	269268.6	4.359	8.87
	C 1s	284.39	2.801	142005.0	0.278	69.83
	Se $3d_{5/2}$	53.69	2.709	21562.0	0.853	2.98
OLC intercalated $\text{In}_4\text{Se}_3(\text{Cu})$ crystal surfaces	Cu $2p_{3/2}$	930.59	2.072	5475.5	3.547	0.22
	O 1s	530.99	2.963	102236.0	0.780	18.35
	In $3d_{5/2}$	443.99	2.881	263790.1	4.359	8.61
	C 1s	284.39	2.801	142000.0	0.278	69.85
	Se $3d_{5/2}$	53.71	2.709	21567.1	0.853	2.97

ted photoelectron, i.e., for Se (0.853), In (4.359), Cu (3.547), C (0.278) and O (0.78). The peak areas are those above the linear background. The chemical shifts ΔE_C which are the differences between the binding energy values of XPS lines in the interfaces (see Table 1) and those for free ΔE_0 Se $3d_{5/2}$ 55.2 eV; In $3d_{5/2}$ 443.4 eV; C 1s 284.5 eV; O 1s 530 eV cannot be easily used to calculate the charge transfer Δq in the $\text{In}_4\text{Se}_3\text{-C,O}$ interface, as well as in the case of Se-C or In-O. These shifts appear to be due to different chemical environments caused by rearrangement of the electron charge distribution during the interface formation and might help to estimate the "ionicity" value f_i . The charge transfer from carbon to Se [3] can be calculated using the expression [15, 16]

$$\Delta E_C = 14.4 \cdot \Delta q \left[\frac{A(G)}{r} - \frac{\alpha_M}{R} \right], \quad (2)$$

where α_M — is the Madelung constant of In_4Se_3 and $\text{In}_4\text{Se}_3\text{-C}$ interface "lattice" (unknown), respectively. $A(G)$ is the geometrical factor amounting 2.77 for II-VI compounds and (unknown) for III-VI compounds; r , the nearest neighbor spacing of "cations" (2.78–3.36 Å) and R , the nearest "anion" distance from the "cation". The ionicity f_i was calculated using the Δq value as [17]

$$\Delta q = -[Z - 4(1 - f_i)], \quad (3)$$

where Z is the valence charge of "cation" in the system $\text{In}_4\text{Se}_3\text{-C}$, (Se-C). All these parameters, viz. ΔE_C , Δq and f_i now cannot be calculated for the $\text{In}_4\text{Se}_3\text{-C}$ interface system.

The chemical shifts $\Delta E_C = \Delta E_0 + W$. The values of work function W which might be used in the calculations of ΔE_C are changing in the $\text{In}_4\text{Se}_3\text{-C}$ interface system and depend on the carbon coverage degree θ ($\Delta W = f(\theta)$). Besides, it is necessary to know the work functions for In_4Se_3 , In, Se, and C. There are no precise values of work functions that could be used to calculate ΔE_C and other parameters (α_M , $A(G)$, r and R) for calculation of Δq .

The interlayer surfaces were obtained by cleavage of In_4Se_3 crystals in the UHV chamber of AES spectrometer (09IOS-2 type) equipped with a MX-7304A mass-spec-

trometer ($P_{\text{CO}} = 6.7 \cdot 10^{-7}$ Pa). It is well known that the unit cell at the atomically clean surface of In_4Se_3 ultrahigh vacuum cleavage contains 7 Se atoms and 15 (16) In atoms (Fig. 1) [2, 13] and there are 20 atoms at the adsorbing surface (7 Se atoms and 13 In ones). Then, it must be supposed that the surface coverage degree with carbon is at least $\theta \cong 7:20 = 0.35$ (after 1 h exposure to UHV residual gases), when I_C/I_{Se} kinetics attains saturation [3, 4, 13], i.e., all Se sites are covered by carbon (Se-C). Probably in the course of the consequent covering of the surface with carbon, CO adsorption occurs on the surface In atoms that are single-ionized (In^+). The calculated values of effective escape depth for $\text{In}_4\text{Se}_3\text{-C}$ interface system: $\lambda_{\text{C}(272 \text{ eV})} = 4.0 \text{ \AA}$; $\lambda_{\text{In}(404 \text{ eV})} = 8.5 \text{ \AA}$; $\lambda_{\text{Se}(1315 \text{ eV})} = 15 \text{ \AA}$ [13]. The thickness of graphite monolayer is considered to be $d_a = d_C = 3.35 \text{ \AA}$ [18].

The AES quantitative analysis of adsorbed layer on the surface of In_4Se_3 cleavages was conducted by method of pure elemental standards [11]

$$C_n = \frac{I_n/S_n}{\sum_j I_j/S_j}, \quad (4)$$

where C_n is the n -th element concentration (i.e., ratio of volume density of element n to general volume density of all elements present in the sample); I_j , intensities of elemental Auger peaks; and S_j , the elemental sensitivities. Such analysis is not quite correct even considering matrix corrections (when sensitivities S_j are obtained from samples with a composition different from the studied ones). The elemental sensitivity factors [19] are as follows: for In, $S_{\text{In}(404 \text{ eV})} = 0.76$; Se, $S_{\text{Se}(1315 \text{ eV})} = 0.08$; C, $S_{\text{C}(272 \text{ eV})} = 0.13$; O, $S_{\text{O}(508 \text{ eV})} = 0.50$.

The application of standard method of quantitative Auger analysis with matrix corrections [19] using the well-known volume elemental sensitivity factors gives a good agreement with stoichiometric crystal composition for atomically clean In_4Se_3 surface. The calculations give values of 57.11 % for In and 42.89 % for Se, that are homogeneous over the whole UHV cleavage surface, and In_4Se_3 stoichiometry composition is: In — 57.14 %, Se — 42.86 %. Table 2 shows the surface elemental concentrations in the case of CO adsorption kinet-

Table 2. Arbitrary concentrations of the surface components for atomically clean surface (ACS), FRC and OLC surfaces of In_4Se_3 crystals obtained by XPS and AES methods

Crystal. In_4Se_3 -C,O interface system		Arbitrary concentrations of the surface components, at %			
		In	Se	C	O
XPS	(FRCs) In_4Se_3 -C,O	36.44	16.46	34.57	12.53
	(OLCs) In_4Se_3 -C,O	8.66	2.98	69.83	18.32
AES	(ACS) In_4Se_3	57.11	42.89		
	(UHV) In_4Se_3 -C	32.50	5.10	62.40	
	(FRCs) In_4Se_3 -C,O	8.32	3.39	86.86	1.43
	(OLCs) In_4Se_3 -C,O	4.07	3.11	91.34	1.48

ics analysis at the UHV cleavages of In_4Se_3 . Obviously, such analysis is not quantitatively precise, however, it allows for some qualitative conclusions (Table 2). The peculiarities of Auger electron emission for adsorbate-adsorbent system as compared to the homogeneous one cause the fact that adsorbed carbon monolayer ($\theta = 1$) defined as such from $I_{\text{C}}/I_{\text{In}}$ and $I_{\text{C}}/I_{\text{Se}}$ kinetics, occurs only about 70 % of surface layer content at the ultrahigh vacuum cleavage of In_4Se_3 when calculated by method of pure standards with matrix corrections. No oxygen adsorbed at the surface is observed at In_4Se_3 interface formed on the UHV cleavages obtained by cleavage of In_4Se_3 in the UHV chamber of AES spectrometer. A negligible amount of adsorbed oxygen is observed on "fresh" and "old" cleavage surfaces exposed to air (Table 2). The investigation of the interface formation processes on the cleavage surface are much more correct than that for the surfaces cleaned by acid and brushed with Alconox with further treatment sequentially in acetone and ethanol using an ultrasonic cleaner. The registrations in the last case, without extra in situ preparation, always show high carbon concentrations at least of 15–20 at. % [6]. Therefore, the studies of the cleavages obtained in UHV Auger spectrometer chamber and in the air allow for correct conclusions on the interface formation at the surfaces of layered semiconductor In_4Se_3 crystal.

Thus, the XPS analysis of the layered semiconductor In_4Se_3 crystal cleavage surfaces exposed to air have been conducted. The peculiarities of interfacial carbon layer formation at the cleavage surfaces of the crystals, elemental composition of the interface dependent on air exposure time have been studied by quantitative XPS methods. The quantitative electron spectroscopy of the interface layer formation at the cleav-

age surfaces of the crystals has revealed a high adsorption of CO at In_4Se_3 surfaces and interface carbon layer formation. The different approaches to quantitative analysis of In_4Se_3 -C,O interface layer formation allow to obtain the compound yields. The formation of In-In metallic binding and metallic phase at the free cleavage surfaces of In_4Se_3 and Cu-In-Se bindings for In_4Se_3 (Cu) intercalated crystals (the Cu $2p_{3/2}$, In $3d_{5/2}$, Se $3d$ binding energies are close to ones for CuInSe_2) have been found.

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Рентгенівська фотоелектронна спектроскопія міжфазових меж на поверхнях сколювання напівпровідникових шаруватих кристалів In_4Se_3

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Представлено результати дослідження формування міжфазових меж на поверхнях сколювання кристалів шаруватих напівпровідників In_4Se_3 , $\text{In}_4\text{Se}_3(\text{Cu})$, одержані методом рентгенівської фотоелектронної спектроскопії. Особливості цього процесу в атмосфері залишкових газів надвисоковакуумної камери досліджено методом оже-електронної спектроскопії. Вуглецево-кисневі інтерфейсні покриття на міжшарових поверхнях сколювання формуються у результаті взаємодії повітря з атомно чистими поверхнями сколювання кристалів.