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## **Electronic energy structure of the (100) In<sub>4</sub>Se<sub>3</sub> surfaces at different preparation and treatment in ultraviolet photoelectron spectroscopy study**

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The (100) surface of In<sub>4</sub>Se<sub>3</sub> layered crystal was obtained *in situ*, ions sputtered and exposed to UHV for hours. The UPS spectra for these surfaces, atomically clean, and after the mentioned treatments, were recorded and analyzed to obtain electronic spectra of In<sub>4</sub>Se<sub>3</sub> (100) surface. The first-principles calculations were performed by DFT-GGA method, and for the In<sub>4</sub>Se<sub>3</sub> underestimated (0.21 eV) band gap was attained. The calculated total density of states of In<sub>4</sub>Se<sub>3</sub> in general coincides with a UPS spectrum for an atomically clean cleaved surface. Thus the study of the band structure of (100) In<sub>4</sub>Se<sub>3</sub> cleavage surfaces after the ion sputtering or exposure to UHV for more than several hours is uninformative, and such effects on the sample should be avoided.

**Keywords:** layered crystals; ultraviolet photoelectron spectroscopy; band structure; generalized gradient approximation.

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### **Introduction**

Layered structures with weak WdW bonding between the layers and strong covalent-ionic interaction within the layer are the objects of continuous investigations, as they give one ability to deeper understand the properties of 2D-structures. Layered In<sub>4</sub>Se<sub>3</sub> crystals, due to their crystalline structure and furrowed on atomic scale cleavage (100) surfaces, have a perspective of usage as a source of natural nanoclusters of nanowires at these surfaces [1, 2], or can be a natural anisotropic surfaces with anisotropic electron spectra [3].

Methods of Ultraviolet Photoelectron Spectroscopy (UPS) and Angle Resolved Ultraviolet Photoelectron Spectroscopy (ARUPS) are known to provide a direct information on band structure and surface states' density [4]. Then investigating cleavage surfaces (100) of In<sub>4</sub>Se<sub>3</sub> by means of these spectroscopies, one can obtain the spectra with possible manifestations of electronic anisotropy, and particular surface electronic states, participating in adsorption and interfaces formation on the studied surface.

Previously, it was shown, [5] by means of low-energy electron diffraction that the lattice of the crystal is not rearranged after the cleavage, so the (100) surface is structurally stable. Thus, atomically clean (100) surfaces In<sub>4</sub>Se<sub>3</sub> do not undergo reconstruction. This conclusion allows us to carry out ARUPS to investigate electron spectra anisotropy. Nevertheless, the question about (100) In<sub>4</sub>Se<sub>3</sub> cleavage surfaces electron spectra is not trivial, since these surfaces, inertial and stable structurally, may not be that inertial from the point of the adsorption, especially after cleavage and air exposure, or UHV-cleavage and ions sputtering.

Thus the question arises – how the surface treatment (for example, ions sputtering, exposure at different conditions or VUV-irradiation) will influence UPS spectra and, accordingly, electronic spectra of (100) surface In<sub>4</sub>Se<sub>3</sub>? This work aims at finding out, how the different methods of cleavage surface cleaning will affect the electronic spectra of (100) surfaces of In<sub>4</sub>Se<sub>3</sub>, obtained by UPS.

## I. Experimental details

### Materials

The In<sub>4</sub>Se<sub>3</sub> layered crystals were grown by Czochralski method. The samples under investigation with 3×6×4 mm<sup>3</sup> in size, had special cleavage-suitable form, and were under cleavage in UHV chamber at room temperature with microtome stainless blade.

### Methods

The UPS study allows to obtain directly and with high energy resolution the N(E) density of states for the valence electrons and electron density for the core-levels from the experimental photoemission energy spectra, i.e., the band structure of the surface. These spectra depend on the final-state energy or the exciting quanta energy. That's why if the final-state energy increases, the energy resolution is decreased due to many-electrons and electron-phonon interactions and thus significant background in the spectra arises.

Most photoelectrons, emitted with characteristic energy, come out of a few surface layers of the layered crystal, and that's why the interfaces formation on the (100) In<sub>4</sub>Se<sub>3</sub> cleavage surfaces significantly affects the low-energy part of the UPS spectra, as well as the states at the valence band top [6].

The first step to determine the appropriate experimental conditions for the band structure and electron energy spectra of the cleavage surfaces studies, is to analyse the interfaces formation *in situ*: at the cleavage surfaces, immediately after the cleavage, on residual gases atmosphere exposure, on ion sputtering, and after "white" VUV irradiation. Moreover, these characteristics might be uncontrolled influenced by interface layers [7, 8], what is an additional purpose of the study.

### Instruments

The experiments were carried out at the Center for Microstructures and Devices (CAMD) Synchrotron Light Source at Louisiana State University. For the experiments was used synchrotron polarized radiation, decomposed into a spectrum with 3 m toroidal grating monochromator – 3 m TGM,  $h\nu \geq 15$  eV and 3 m normal incidence monochromator – 3 m NIM.

The UPS research was carried out using monochromatic synchrotron radiation, which irradiated

the sample in the UHV chamber of the slot end station. The end station consisted of an UHV system with ion pumping and residual gas pressure of  $1.5 \times 10^{-10}$  Torr. The atmosphere of the UHV contains residual gases, mainly CO, H<sub>2</sub>O and H<sub>2</sub>, as well as a small amount of hydrocarbons (partial pressures less than  $10^{-12}$  Torr).

The combined resolution of the electron energy analyzer and monochromator is 120-150 meV (for photon energies 50-120 eV), but higher resolution, about 80 meV, is obtained at lower photon energies of 15–40 eV.

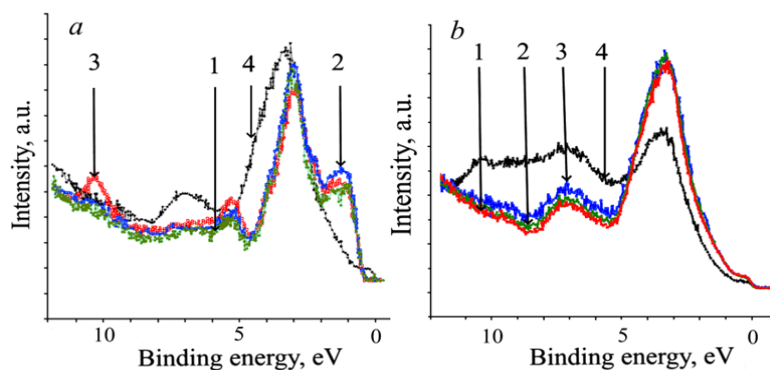
The high resolution (9-10 meV) photoemission studies were carried out on the 3 m normal incidence beamline for  $h\nu \geq 4$  eV that consists of water cooled ellipsoidal entrance mirror, electron energy analyzer Scienta SES200, and a magnetic field shielded UHV chamber [9].

VUV photons with the energy range of 15-110 eV were used in UPS studies. All electron binding energies of the (100) In<sub>4</sub>Se<sub>3</sub> cleavage surface are referenced to the Fermi level, as determined from clean gold (work function 5.3 eV [10], and for the atomically clean (100) In<sub>4</sub>Se<sub>3</sub> surface it is equal to 4.3 eV).

## II. Results and Discussion

Different (100) In<sub>4</sub>Se<sub>3</sub> surfaces were studied by the UPS: obtained *in situ* atomically clean immediately after cleavage, exposed in the residual gases atmosphere of the UHV chamber, as well as surfaces after the ion sputtering. Thus, changes in the density of electronic states of the valence band and core (In 4d and Se 3d) levels during the formation of the interface on the (100) In<sub>4</sub>Se<sub>3</sub> cleavage surface were studied.

Fig. 1 presents the obtained UPS spectra of the electrons' density of states, obtained in the normal emission mode. All given spectra are normalized to the emission excitation photon fluxes. On the figures, it is possible to observe a significant changes in the UPS spectra after the cleavage surfaces ion sputtering, for example, a broad maximum in the low-energy (1-2 eV) region has disappeared and a slight (0.3-0.4 eV) shift of the Fermi level is observed (Fig. 1a, compare curves 1 and 4).



**Fig. 1.** The UPS spectra of (100) In<sub>4</sub>Se<sub>3</sub> cleavage surfaces ( $h\nu = 25$  eV, emission normal to the cleavage surface):  
*a* – 1 - atomically clean surface just after the cleavage in UHV; 2 – after cleavage *in situ* and UHV exposure for 5 h; UHV exposure for 12 h; just after ion sputtering Ar<sup>+</sup> ( $E = 1.6$  keV,  $I = 10$   $\mu$ A,  $P_{Ar} = 5 \times 10^{-5}$  Torr);  
*b* – 1 – 15 min after ion sputtering and UHV exposure; 2 – 1 h after ion sputtering and UHV exposure; 3 – 10 min additional ion sputtering in UHV; 4 – 30 min additional ion sputtering in UHV and 12 h UHV exposure ( $10^{-9}$  Torr).

We can see that the UPS spectra of (100)  $\text{In}_4\text{Se}_3$  cleavage surfaces, cleaned of interface coatings with  $\text{Ar}^+$  ions are significantly different when compared to the spectra obtained for atomically clean surfaces (Fig. 1a, curves 1 and 4). The sputtering coefficient for Se atoms with  $\text{Ar}^+$  ions is approximately 1.1 times higher than for In, so as a result of ion sputtering, the cleavage surface is enriched with In atoms. As a result, one can see the changes at the UPS spectrum of the valence band electrons density of states, Fermi level shifts and, accordingly, the work function changes ( $\approx 4.3$  eV for  $\text{In}_4\text{Se}_3$  and  $\approx 3.8$  eV for metallic In), which leads to the shifts in electrons binding energies.

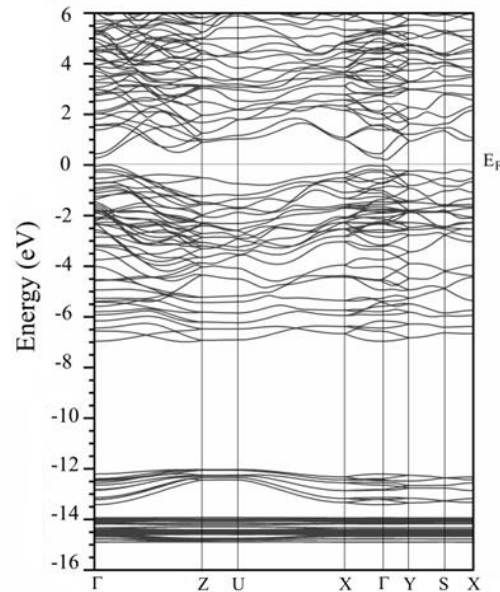
UPS spectra of (100)  $\text{In}_4\text{Se}_3$  cleavage surfaces after the ion sputtering and UHV exposure (Fig. 1b), demonstrate a significant irreversible changes of peak intensities and binding energies, i.e., changes in the density of states of the surface valence band. It is obvious, that as a result of the effects of differential sputtering, the elemental composition of (100)  $\text{In}_4\text{Se}_3$  cleavage surfaces is changed so much, that they are no longer suitable for the band structure analysis and for the investigation of electronic spectra of clean undamaged cleavage surfaces. In addition, from Fig. 1b one can see, that the density of states on such surfaces depends on the ion sputtering conditions, as well as on the treatments and "storage" of the surfaces even in UHV.

Two peaks (at 1 eV and 3 eV approximately) are characteristic for an atomically clean surface and are due to the In-s, In-p and Se-p states of valence band, and are extended to the bond energies  $-5$ – $-5.5$  eV [11]. Here one can observe significant changes in the spectra of the electrons emitted from the valence band energy states, created by the Se-p states (with the binding energy  $\approx 1$  eV), which is also observed on the Fig. 1. That is, there is a decrease in the intensity of photoemission from Se-p-states due to adsorption, particularly CO, primarily on selenium atoms of the surface (Se1, Se2, Se3).

On Fig. 1a, in addition to the above, it is possible to observe (curve 4) a significant changes in the UPS spectrum after sputtering the surface (100) with  $\text{Ar}^+$  ions: the "selenium" peak disappears and a slight energy shift of the Fermi level is seen. Since, in a result of the sputtering, the cleaved surface (100) is enriched with In atoms, the UPS spectrum of the valence band electrons density of states (binding energy  $\approx 3.5$  eV) caused by the indium component (In1, In2, In3), and especially In4 (binding energy  $\approx 1$  eV, Fig. 1), changes.

The first-principles calculations were performed by DFT-GGA method (Density Functional Theory-Generalized Gradient Approximation) with the adopted generalized gradient approximation implemented by Perdew, Burke, and Ernzerhof (PBE [12]) for the exchange correlation energy functional without the spin-orbit interaction. The  $1 \times 1 \times 4$  Monkhorst and Pack scheme of k-point sampling is used for integration over the first Brillouin zone. The energy cutoff is chosen to be 395 eV. The unit cell is composed of 28 atoms with seven different sites (four sites for indium atoms and three sites for selenium ones) and each site occupies four equivalent atomic positions. The lattice parameters for calculations are  $a = 15.296$  Å,  $b = 12.308$  Å, and  $c = 4.0806$  Å in the orthorhombic space group Pnnm [13].

Band structure of the layered crystal  $\text{In}_4\text{Se}_3$  for the first reduced Brillouin zone in the high-symmetry direction  $\Gamma$ -Z-U-X- $\Gamma$ -Y-S-X is drawn on the Fig. 2. This structure can be considered as having five main packages - four below the Fermi level (binding energy up to 15 eV) and one above - conductivity band states.

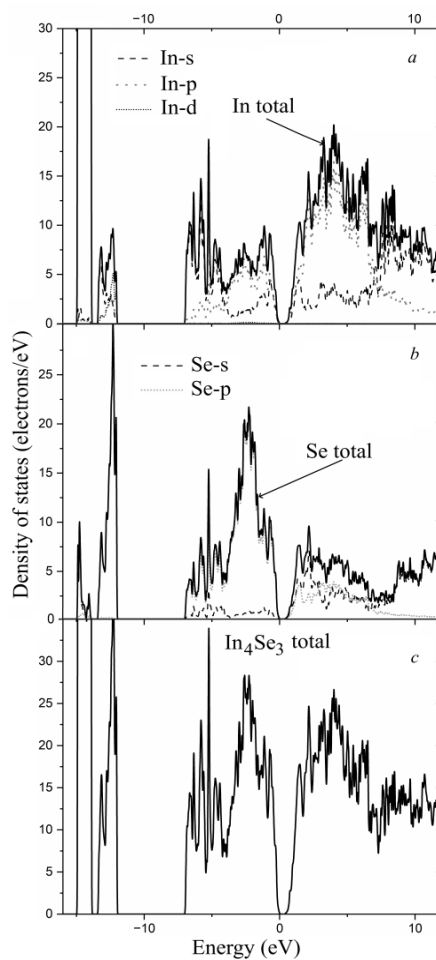


**Fig. 2.** Band structure and electron spectra of the  $\text{In}_4\text{Se}_3$  layered crystal for the first reduced Brillouin zone (high-symmetry direction  $\Gamma$ -Z-U-X- $\Gamma$ -Y-S-X). The electronic configurations for In and Se for the calculations were  $49\text{In}[\text{Kr}^{36} 4d^{10}] 5s^2 5p^1$ ;  $34\text{Se}[\text{Ar}^{18} 3d^{10}] 4s^2 4p^4$ .

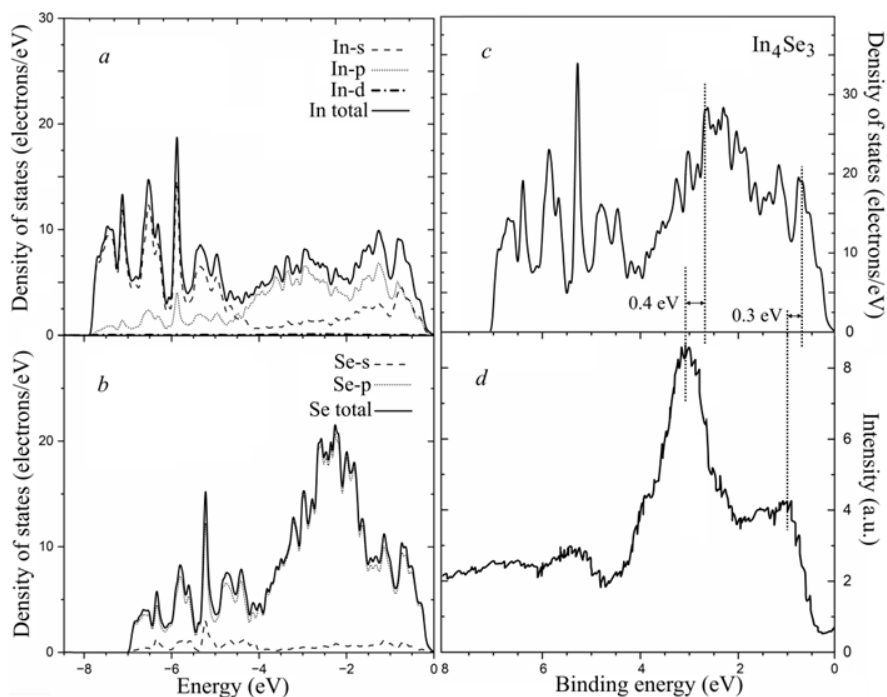
From our calculations the band gap for  $\text{In}_4\text{Se}_3$  is 0.21 eV. In the [14], from first principles by the pseudopotential method, for the energy gap between the top of the valence band and the bottom of the conductivity band, was attained  $\approx 0.3$  eV. The other sources [15, 16] have the experimental results 0.42–0.86 eV. Note that the discrepancy between DFT-GGA-calculated  $E_g$  value and experimental results is nothing special, because DFT-GGA, as a rule, underestimates  $E_g$ . However, the initial material data predicts that the surface is more non-conductive than the bulk, or at least its band gap is wider (not less) than for the bulk.

The "lowest" flat, isotropic band is due to In-4d states ( $-15.00$  ÷  $-13.73$  eV). Next comes the dispersion band due to Se-4s and also, however, weaker, In-4d states ( $-13.59$  ÷  $-11.91$  eV). It is followed by the band gap, which extends from  $-11.91$  to  $-7.17$  eV below the Fermi level and to the beginning of the valence band bottom. The In-5s and In-5p states dominate in the peaks of the valence band, however, at energies  $-1.5$  eV, the Se-4p and In-5p states dominate the valence band, as it can be seen from Fig. 3.

From the Fig. 3a, b it could be seen, that the conductivity band of  $\text{In}_4\text{Se}_3$  is mainly due to In-p and Se-p orbitals, although the contribution of In-p orbitals is a little more. A similar situation with a sharp change in the density of In-s and Se-p "states" is observed near the top of the valence band (Fig. 4a, b), with a greater contribution of Se-p states.



**Fig. 3.** Partial contributions of the orbitals of In (*a*) and Se (*b*) atoms of the layered crystal  $\text{In}_4\text{Se}_3$  to the density of states of the valence band, and the total density of states of the valence band at the low binding energies (*c*).



**Fig. 4.** Calculated partial contributions of In (*a*) and Se (*b*) atoms orbitals to the density of occupied and free states with low binding energies, and total density of states of  $\text{In}_4\text{Se}_3$  (*c*) in comparison with a fragment of the UPS spectrum (*d*) ( $h\nu = 15$  eV; angle of incidence  $\Psi = 45^\circ$ ; emission normal to cleavage surface (100)  $\text{In}_4\text{Se}_3$ ) for the corresponding range of bond energies.

In particular, In-s cationic states hybridized with cationic In-p (5s1p2) and anionic (Se-s, -p) partners and forming bonds are very important for the electronic properties of the (100) In<sub>4</sub>Se<sub>3</sub> cleavage surface. The reason for this the fact, is that they determine the In<sub>4</sub>Se<sub>3</sub> band gap, and possibly appear as quasi-local states (Se-p, In-s, -p).

Note that according to the results presented on Fig. 4, valence band in the range of binding energies -2.5 ÷ -4.5 eV is mainly due to In-5p and Se-4p states. The calculated densities of occupied states in the valence band region agree satisfactory with the results of the UPS (Fig. 4d). Therefore, even in the UHV conditions, In<sub>4</sub>Se<sub>3</sub> cleavage surfaces are not inert to the gas adsorption. The transformations of the peaks at ≈ 1 eV and ≈ 3 eV in the UPS spectra during the adsorption of the UHV chamber residual gases, is the argument that allows one to associate these changes with the presence of surface electronic states, energetically located in the valence band and associated with the dynamic changes of the electron density of Se-p states.

The presence of interfaces formed on the (100) In<sub>4</sub>Se<sub>3</sub> surfaces, obtained by cleavage, both in the air and in the UHV, significantly affects the UPS spectra. On the other hand, for the atomically clean surfaces, the largest changes in the spectra occur during their long-term exposure (over 50 L) in the atmosphere of UHV chamber residual gases, although smaller changes are observed during the subsequent VUV irradiation (15 ÷ 350 eV).

Therefore, reliable results of UPS for the band structure, electron spectra E(k) and nanotechnological manipulations on atomically clean (100) In<sub>4</sub>Se<sub>3</sub> surfaces are possible to obtain, when the surfaces are exposed to UHV up to approximately 2 L, but the cleaved surfaces are still “sufficiently clean” up to 12-13 L in UHV. UPS spectra of (100) In<sub>4</sub>Se<sub>3</sub> cleavage surfaces after the interface coatings sputtering with the ions Ar<sup>+</sup>, are significantly different when compared to the spectra of the surfaces, obtained and exposed in UHV. It is obvious that

neither the first, nor the second are suitable for the investigations of the band structure or electronic spectra E(k) of crystal cleavage surfaces.

## Conclusions

The obtained results allow us to state that the study of the band structure of (100) In<sub>4</sub>Se<sub>3</sub> cleavage surfaces after the ion sputtering or exposure to UHV for more than several hours, is uninformative. With such treatments of the cleavage surfaces (ion sputtering or exposure), it is difficult to establish the dependence of the peak intensity and binding energy on the exposure time. This means that such procedures with (100) In<sub>4</sub>Se<sub>3</sub> cleavage surfaces are not admissible in the study of their electron spectra, as the mentioned influences cause the noticeable shifts in electron binding energies and changes in the valence band density of states for the studied surface. These shifts and intensity changes on the UPS spectra are irreversible, and are intricately related to the exposure and ion sputtering durations, therefore, when studying the energy spectrum of (100) In<sub>4</sub>Se<sub>3</sub> cleavage surfaces, such effects on the sample should be avoided.

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## Електронна енергетична структура поверхні (100) $\text{In}_4\text{Se}_3$ за різного приготування та при різних впливах при дослідженні ультрафіолетовою фотоелектронною спектроскопією

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Поверхні (100) шаруватого кристалу  $\text{In}_4\text{Se}_3$  отримувалися *in situ*, розпилювалися іонами та витримувалися у НВВ протягом кількох годин. Спектри УФЕС таких поверхонь, атомарно чистих та після згаданих впливів, записувалися та аналізувалися задля отримання електронного спектру поверхні (100)  $\text{In}_4\text{Se}_3$ . Першопринципні розрахунки зонної структури проводилися у наближенні узагальненого градієнту теорії функціонала густини, і для  $\text{In}_4\text{Se}_3$  отримано занижену оцінку (0.21 eV) для забороненої зони. Розрахована повна густина станів  $\text{In}_4\text{Se}_3$  в цілому співпадає з УФЕС спектром для атомарно-чистої поверхні. Тому вивчення зонної структури поверхні сколу (100)  $\text{In}_4\text{Se}_3$  після іонного розпилення чи перебування у НВВ більше, ніж кілька годин, слід вважати неінформативним, і таких впливів на зразок слід уникати.

**Ключові слова:** шаруваті кристали, ультрафіолетова фотоелектронна спектроскопія, зонна структура, наближення узагальненого градієнта.