

Anisotropy of the electron spectra of the cleavage surface (100) of layered In_4Se_3 crystals

Pavlo V. GALIY^{1*}, Taras M. NENCHUK¹, Ostap R. DVERIY¹, Yaroslav B. LOSOVYJ²

¹ Faculty of Electronics, Ivan Franko National University of Lviv, Dragomanova St. 50, 79005 Lviv, Ukraine

² The Bennett Johnston Sr. Center for Advanced Microstructures and Devices, Louisiana State University, 6980 Jefferson Highway, Baton Rouge, LA 70806, USA

* Corresponding author. Tel.: +380-32-2394678; e-mail: galiy@electronics.wups.lviv.ua

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It is shown from angle resolved ultraviolet photoemission spectroscopy that the ordered surfaces of the In_4Se_3 (100) system exhibit anisotropy of the electron spectra (*i.e.* discernable and significant valence band dispersion), both parallel and perpendicular to the cleavage plane. Parallel to the cleavage plane, the electron spectra differ along the crystallographic axes *b* and *c*. Band widths (extent of dispersion) of $\cong 1$ eV are observed along the surface chain rows and about 0.5 eV perpendicular to the surface “furrows”. The downward dispersion (towards greater binding energy) of the band at the valence band maximum, away from the Γ point, can be understood since this band is dominated by In-*s* and Se-*p_y* bonds. The band widths of 0.3 to 0.4 eV perpendicular to the chain direction (Γ -Y) and 1.25 eV along the chain direction (Γ -X), for bands within the valence region, are in line with the expectations from the calculated band structure.

Layered crystals / Angle resolved ultraviolet photoemission spectroscopy / Electron spectra / In_4Se_3

Introduction

In_4Se_3 semiconductor crystals form a layered structure characterized by, in principle, weak interactions of van der Waals type between the layers and strong covalent-ionic interactions within the layers, but the (100) surface is not “smooth” (see cleavage (100) surface of a single layer on Fig. 1a). The quasi two-dimensionality (2D) of the layered crystals and, consequently, absence of free unsaturated electron bonds at the cleavage surfaces, does not really apply here as the layers are not flat but corrugated, resulting in a quasi one-dimensional (1D) chain structure at the semiconducting (100) In_4Se_3 surface. In_4Se_3 is, in fact, dominated by $(\text{In}_3)^{5+}$ multivalent clusters bonded to selenium through ionic-covalent bonds (see chainlike structures on Fig. 1b).

The layered crystal structure of In_4Se_3 allows obtaining (100) cleavages [1,2]. The surface of In_4Se_3 provides an opportunity to study the electronic structure of In chains in the presence of strong bonding with Se atoms. Here we show that the In_4Se_3 (100) surface is characterized by a clear band structure (*i.e.* discernable and significant band dispersion) along the chain direction, with a weak but nonetheless noticeable dispersion perpendicular to both the chain direction and the cleavage plane.

Most photoelectrons issued with characteristic energetic spectra originate from a few atomic layers of the crystal and the formation of interfaces on the surface of In_4Se_3 cleavages substantially influences the ultraviolet photoemission spectroscopy (UPS) spectra of the surfaces. The analysis of the formation of interfaces on *in situ* cleavages, directly after cleavage and exposition to the atmosphere of residual gases, and after such treatments as ionic sputtering and ultraviolet irradiation, is the first step of experimental studies of the local structure and electronic spectra of crystal surfaces. Besides, such an analysis is useful for detecting probable uncontrolled influences on the interface layers.

Experimental

The crystals were grown by the Czochralski method and then cleaved *in situ*. The surface order was established by low-energy electron diffraction and scanning tunneling microscopy (STM) [3]. The crystal structure of In_4Se_3 was found to be in agreement with prior structural determinations, with the refined lattice constants $a = 15.297(1)$ Å, $b = 12.308(1)$ Å, $c = 4.0810(5)$ Å in the orthorhombic space group *Pnmm*, obtained by X-ray diffraction using $\text{Cu } K_\alpha$ radiation.

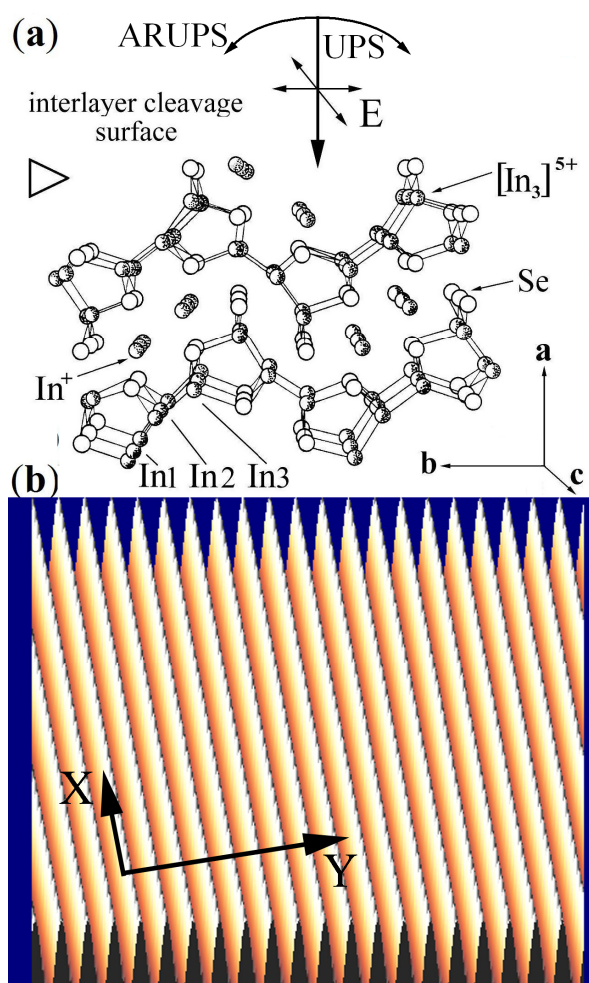


Fig. 1 (a) Schematic crystal structure of In_4Se_3 . The lattice constants of the crystal structure are: $a = 15.297(1) \text{ \AA}$, $b = 12.308(1) \text{ \AA}$, $c = 4.0810(5) \text{ \AA}$; space group $Pn\bar{m}$; the structure is dominated by $(\text{In}_3)^{5+}$ multivalent clusters bonded to selenium through ionic covalent bonds. The cleavage direction is indicated by the triangle in the upper left; (b) STM image of a $30 \times 30 \text{ nm}^2$ crystal fragment of the interlayer cleavage (100) surface of In_4Se_3 , corresponding to the crystal structure (a) and 2D/3D In chain along the x direction (lattice spacing c) is indicated.

These values are in agreement with published values. The interlayer cleavage plane (100) of In_4Se_3 is normal to the crystallographic axis a and the layers (see on Fig. 1a). The two-dimensionality of layered crystals does not quite apply to this system as the layers are not perfectly flat but corrugated, resulting in an “1D” chain structures at the In_4Se_3 (100) surface. The chainlike and furrowed (100) surface structure is seen on Fig. 1b.

Angle resolved ultraviolet photoemission spectroscopy (ARUPS) along the chain direction was obtained using plane polarized synchrotron light dispersed by a 3m toroidal grating monochromator, at

the Center for Microstructures and Devices (CAMD). The measurements were conducted in an ultra high vacuum (UHV) chamber employing a hemispherical electron analyzer with an angular acceptance of $+1^\circ$. The combined resolution of the electron energy analyzer and monochromator is about 80 meV at the lower photon energies of 15-40 eV. The photoemission experiments were undertaken with a light incidence angle of 45° with respect to the surface normal and with the photoelectron emission angle indicated where it is appropriate. All binding energies are referenced to the Fermi level, as determined from pure gold. For the band dispersion perpendicular to the chain direction, the dispersion was significantly smaller and the band mapping measurements were complemented by high resolution photoemission.

Results and discussion

The UPS spectra from In_4Se_3 (100) surfaces after cleaning by Ar^+ ion sputtering ($E = 1.6 \text{ keV}$, $I = 10 \mu\text{A}$, $P_{\text{Ar}} = 5 \times 10^{-5} \text{ Torr}$) differ from the spectra of surfaces cleaved in UHV. The density of surface states for In_4Se_3 (100) depends on the conditions of the ionic sputtering and of the subsequent treatments and expositions of the surfaces in UHV (see Fig. 2). Curve 4 in Fig. 2b shows considerable changes in the UPS spectrum after surface cleaning by ion sputtering, such as: disappearance of the maximum in the range of 1-2 eV binding energies and slight shifting of the Fermi level. It is well-known that the coefficient of Ar^+ ionic sputtering is approximately 1.1 times higher for Se atoms than for In atoms. As a consequence of this differential sputtering the cleaved surface is enriched by In atoms. As a result, the UPS spectrum of the density of states of valence electrons changes; the position of the Fermi level shifts and the work function ($\approx 4.3 \text{ eV}$ for In_4Se_3 and $\approx 3.8 \text{ eV}$ for In) changes, which results in shifts of the binding energies of electrons.

The UPS spectra of In_4Se_3 (100) surfaces after ion sputtering and exposition in UHV allow seeing considerable irreversible changes in the peak intensities and binding energies and, consequently, changes in the density of states of valence electrons. After such surface treatments (ion sputtering and exposition) it is difficult to evaluate the dependence of the peak intensity and binding energy on exposition or the composition and structure of the interface layer. Obviously, cleaning of surfaces by ion sputtering is not suitable for electronic spectra studies by UPS.

In spite of the fact that In_4Se_3 (100) is clearly a semiconductor, the dispersion along the chains, for the bands near the valence band maximum, is quite significant, as noted previously [4,5]. Fig. 3 shows the emission dependence of angle resolved photoemission spectra along the chain direction. From the dispersion of the bands, evident in the photoemission spectra as a function of the emission angle (Fig. 3a), we have been

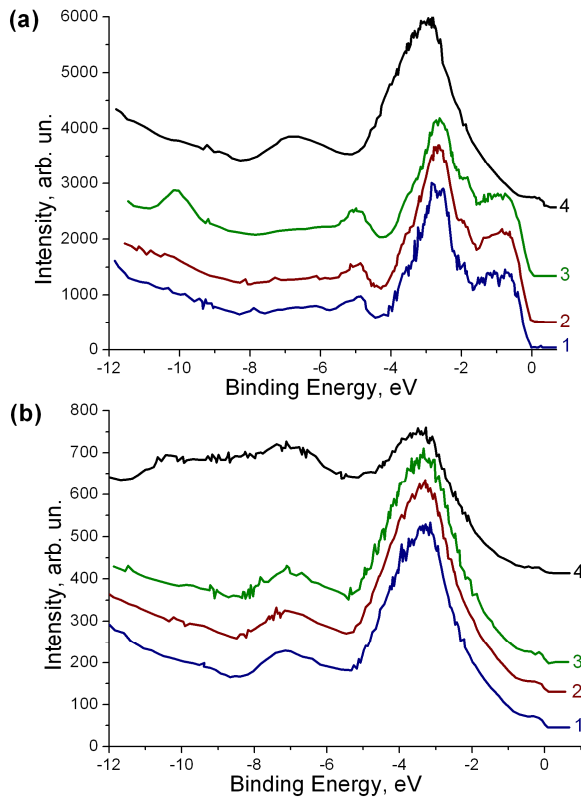


Fig. 2 Ultraviolet photoemission spectra of In_4Se_3 (100) obtained by UHV cleavage ($h\nu = 25$ eV, normal emission): (a) 1 – just cleaved; 2 – after 5 hours; 3 – after a night; 4 – after Ar^+ sputtering ($E = 1.6$ keV, $I = 10$ μA , $P_{\text{Ar}} = 5 \times 10^{-5}$ Torr); (b) 1 – fresh (sputtered 15 min); 2 – after 10 min additional sputtering; 3 – after ~1 hour; 4 – day before (30 min sputtering, one night storage at 10^{-9} Torr).

able to construct a band structure mapping along the Γ -X line (along the surface chains) and Γ -Y line (perpendicular to the surface chains, but in the plane of the surface) using

$$k_{\parallel} = \left[\frac{2m^* E_{\text{kin}}}{\hbar^2} \right] \sin \theta, \quad (1)$$

where k_{\parallel} is the horizontal component of the k wave vector of the emitting photoelectron, m^* the effective mass of the photoelectron, E_{kin} the kinetic energy and θ the emission angle of the photoelectron.

Figs. 3 and **4** show that the dispersion of these bands is somewhat photon energy dependent (**Fig. 3**); some variations of the extent of the band dispersion along the surface chains (with photon energy) occur because the two-dimensionality is not conserved in this otherwise layered system. There exist sufficient interactions between the layers to support a bulk band structure and this is a complication that cannot be ignored.

In any case the band widths (the extent of the dispersion $E(k_{\parallel})$) of 0.30 to 0.40 eV perpendicular to the chain direction (**Fig. 4b**), or 1.25 eV along the

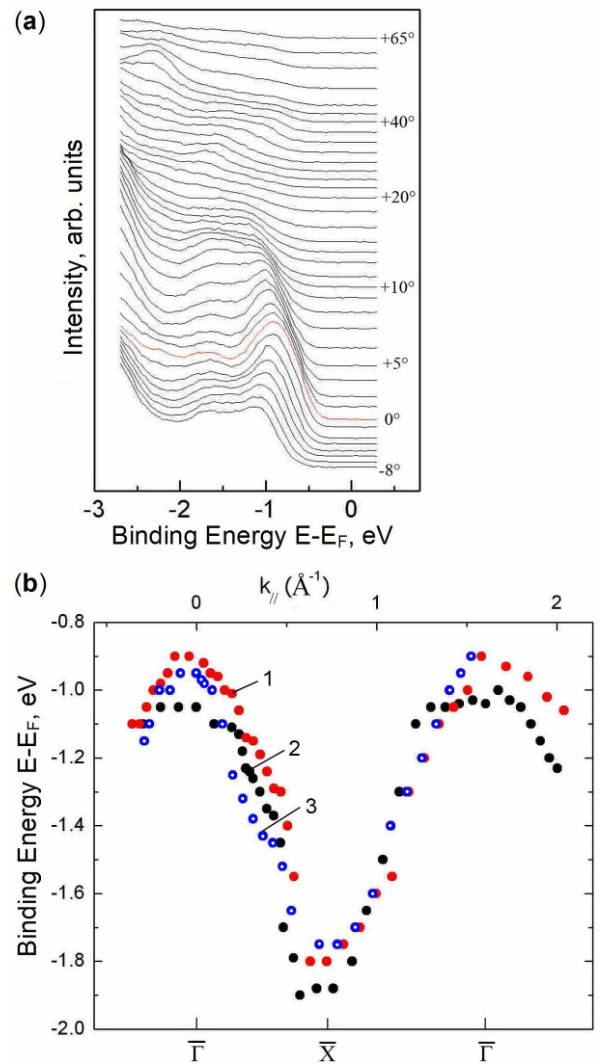


Fig. 3 (a) Angle-resolved photoemission spectra, taken at a photon energy of $h\nu = 25$ eV with k_{\parallel} along the Γ -X direction for In_4Se_3 (100) at 295 K; (b) Experimental band structure along the Γ -X direction in the surface Brillouin zone with the dispersion curves $E(k_{\parallel})$ of the electron valence band: 1 – 295 K, 25 eV; 2 – 80 K, 25 eV; 3 – 295 K, 16 eV [4].

chain direction (**Fig. 3b**), for bands within the valence region, are in line with the expectations from the calculated band structure [6,7] and demonstrate the anisotropy of the surface band structure of layered In_4Se_3 (100).

Conclusions

Cleaved In_4Se_3 (100) surfaces are not inert to gas adsorption, even under UHV conditions. The presence of interface layers, formed on In_4Se_3 (100) surfaces cleaved in air or in UHV, has a substantial influence on the UPS spectra.

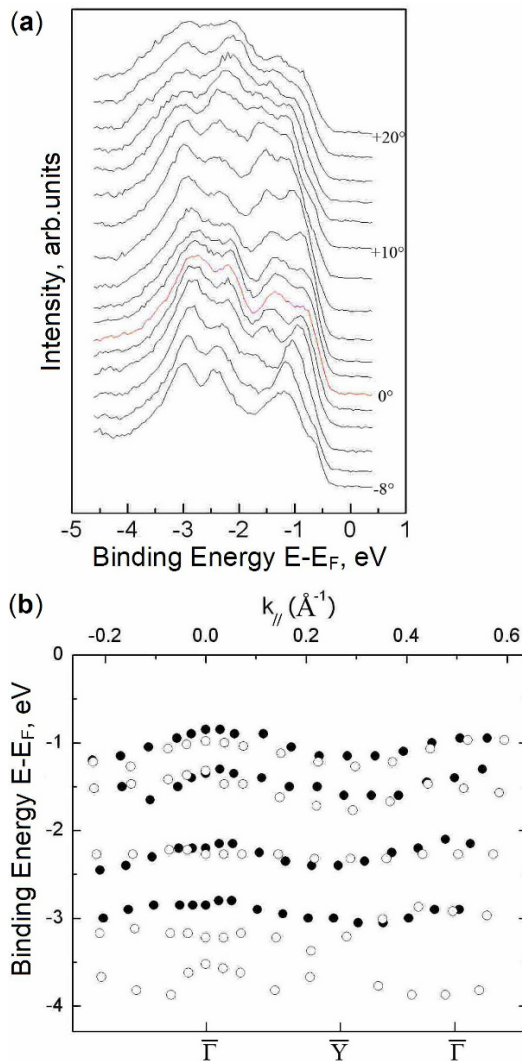


Fig. 4 (a) Angle-resolved photoemission spectra, taken at a photon energy of $h\nu = 15.5$ eV with $k_{//}$ perpendicular to the chain direction, in the Γ -Y direction for In_4Se_3 (100). (b) Experimental band structure along the Γ -Y direction in the surface Brillouin zone with the dispersion curves $E(k_{//})$ of the electron valence band, with critical points and experimental wave vectors identified, measured at two photon energies (15.5 eV – filled circles and 23 eV – open circles) for different binding energies [4].

The ordered surfaces of the layered In_4Se_3 (100) system exhibit a band structure (*i.e.* discernable and significant band dispersion) both parallel and perpendicular to the cleavage plane. Along the principal high-symmetry axes parallel to the cleavage plane, the band structure is consistent with the surface lattice constants $b = 12.3$ Å and $c = 4.08$ Å. Band widths (extent of dispersion) of approximately 1 eV are observed along the surface chain rows, and about 0.5 eV perpendicular to the surface “furrows”, which demonstrates the anisotropy of the surface band structure of the layered In_4Se_3 (100) in this plane.

The downward dispersion (towards greater binding energy) of the band at the valence band maximum, away from the Γ point, can be understood as this band is dominated by In- s and Se- p_y bonds. The band widths of 0.3 to 0.4 eV perpendicular to the chain direction or 1.25 eV along the chain direction, for bands within the valence region, are in line with the expectations from the calculated band structure.

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