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Scanning tunneling spectroscopy of In_4Se_3 layered semiconductor crystals

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The topography and local density of states of the cleavage surfaces of a layered semiconductor In_4Se_3 (100) crystal were analyzed by scanning tunneling microscopy (STM) *in situ*. The shape and dimensions of the acquired STM profiles correspond well to the bulk lattice parameters. The local density of states and band gap for In_4Se_3 (100) were obtained by scanning tunneling spectroscopy (STS), which gave the same gap value as for the bulk crystal. The STM/STS results show a local energetic and phase inhomogeneity of In_4Se_3 (100) cleavage surfaces on the atomic scale. The studies confirm that the furrowed and chainlike surface structure of In_4Se_3 (100) is stable and unreconstructed under the cleavage and might be suitable as an anisotropic, low-conductive matrix/template for fabrication of surface-conductive nanowires or nanostructures.

Scanning tunneling spectroscopy / Scanning tunneling microscopy / Local density of states / Low-dimensional structures / Layered crystals / In_4Se_3

Introduction

It is well known that, due to the relatively weak interlayer bonding, In_4Se_3 layered semiconductor crystal samples cleave along the interlayer spaces. The striking feature of the In_4Se_3 (100) surface is the furrowed and chainlike anisotropic relief, as could be seen after inspection of bulk crystal and energetic structure [1,2]. The approximately two-dimensional (2D) cleavage surface of layered (100)-oriented In_4Se_3 crystals arouses great interest for its potential utilization as template in device fabrication on a nanometer scale, *e.g.* of nanowires [3]. Besides, layered In_4Se_3 crystals have become an attractive subject for practical applications as thermoelectric materials, which exploit intrinsic nanostructure bulk properties induced by charge density waves [4].

The "large" cleavage areas of In_4Se_3 usually show a small number of topographic steps with a height corresponding to the thickness of one or a few layers in scanning tunneling microscopy (STM) images.

STM has the unique ability to reveal structural and electronic information of the surface on the atomic scale. STM images display the geometric structure of the surface, but also depend on the electronic density of states of the sample, as well as on the complex tip-sample interaction mechanisms.

In the present work, we employed STM and scanning tunneling spectroscopy (STS) to study the In_4Se_3 (100) cleavage.

Experimental

Layered crystals of In_4Se_3 (samples of size 3×6×4 mm^3, with a special shape for *in situ* cleavage) were grown by the Czochralski method. In_4Se_3 samples were naturally (through the phenomena of indium self-intercalation) *n*-doped with a carrier concentration of more than 10^{16} cm^{-3}. The samples were cleaved *in situ* at room temperature in an ultra high vacuum (UHV) chamber and in air *ex situ*, using a stainless steel tip. An Omicron NanoTechnology STM/AFM System under UHV ($3\ 10^{-11}$ Torr) was used. An STM/STS investigation of the In_4Se_3 (100) crystal was carried out to yield the topography, *I–V* characteristics, and d*I*/d*V* and normalized d*I*/d*V* *versus* *V*. The STM images were collected in the constant tunneling current mode. To visualize the measured STM and STS data we applied the computer program WSxM v.4.0 designed by Nanotec Electronica [5].

Results and discussion

Since the tip probe is sensitive to locations into (or out of) which electrons can tunnel, STM images are pictures of the local density of states (LDOS) at the surface. These states may, or may not correspond to actual atomic positions. Special care must be taken to isolate the STM from environmental influences such as floor vibrations. Operation under UHV eliminates

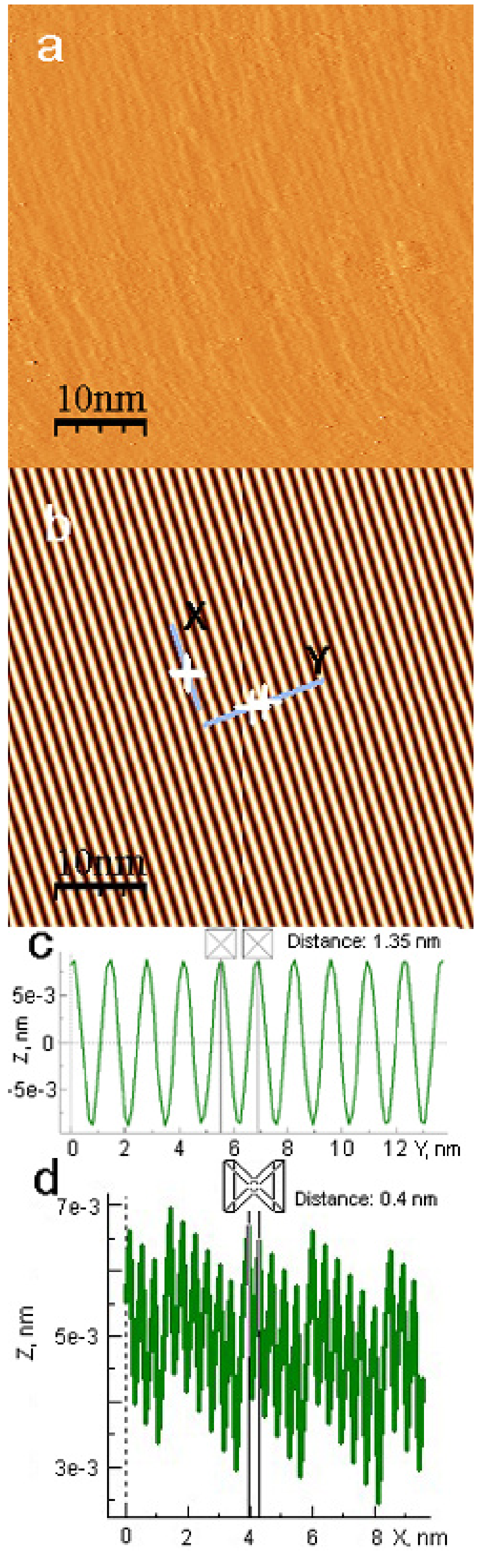

Fig. 1 STM data: (a) Constant current STM image of an In_4Se_3 (100) UHV cleavage surface 50×50 nm^2, acquired with bias voltage +1.5 V; b) Corresponding 2D FFT image with traces of profiling: X – parallel and Y – normal to surface furrows; c), d) Periodical distances measured for the Y and X profile, respectively.

surface contaminates that interfere with the stability of the tunneling process.

We now turn to some remarkable features appearing in In_4Se_3 (100) surface STM images. Figs. 1 and 2 show typical constant current STM images of an In_4Se_3 (100) UHV cleavage surface 50×50 nm^2, obtained with a bias voltage +1.5 V (0.031 nA) (thus corresponding to electrons tunneling from the probe-tip into normally empty states of the sample) and –1.5 V (0.114 nA) (vice versa tunneling). The STM images were filtered applying a 2D Fast Fourier Transform (FFT) to reveal the periodical structure of the surface, and subsequent profiling gave periodicity distances of about 1.3-1.4 nm and 0.4 nm. These values are in good agreement with the lattice parameters normal and parallel, respectively, to the furrows or chains on the cleavage surface, derived by "bulk" (X-ray diffraction) [1] or "surface" (low-energy electron diffraction (LEED), atomic force microscopy (AFM)) studies [3,6].

It was relatively difficult to obtain sufficient lattice resolution when acquiring the STS spectra. This may be due to the presence of intercalated indium, which is not connected with specific lattice sites, on the cleavage plane. The latter can be clearly seen when considering local STS spectra of the UHV cleavages.

We mapped the local differential conductance of the surface simultaneously with topographic measurements. Fig. 3a shows a 2D FFT image of the UHV cleavage that reveals a periodic lattice structure corresponding to the In_4Se_3 (100) surface (Fig. 3b shows the subsequent profile with measured surface distances). Current-imaging-tunneling spectroscopy (CITS) is an STS technique where an *I*–*V* curve is recorded at each pixel in the STM topography. Measuring local CITS curves allows characterizing the variation of the local electronic structure. The d*I*/d*V* *versus* voltage bias $V(dI(V)/dV = f(V))$ curve is proportional to LDOS.

Since the tunneling current in a scanning tunneling microscope only flows in a region with a diameter of ~5 Å, STS is unusual in comparison with other surface spectroscopy techniques, such as ultraviolet photoelectron spectroscopy, which average over a larger surface region. STS measurements, averaged over the whole studied sample surface, revealed mainly semiconductor-like behavior ($I = f(V)$) (see Fig. 3c). But, as shown in Fig. 3d, in local spectra we were able to distinguish regions of slightly different electronic properties, towards metallic-like behavior.

Fig. 4 shows a typical averaged normalized $d(I[a.u.])/d(V[V]) / (I[a.u.]/V[V]) = f(V)$ STS spectrum of an *n*-type In_4Se_3 (100) surface, obtained from a 50×50 nm^2 area of a UHV cleavage. This spectrum was acquired as CITS data and normalized by WSxM software. The conduction band and valence band components in the conductance are clearly seen, and the band edges are marked in the spectrum. We define the band gap as the separation between these band

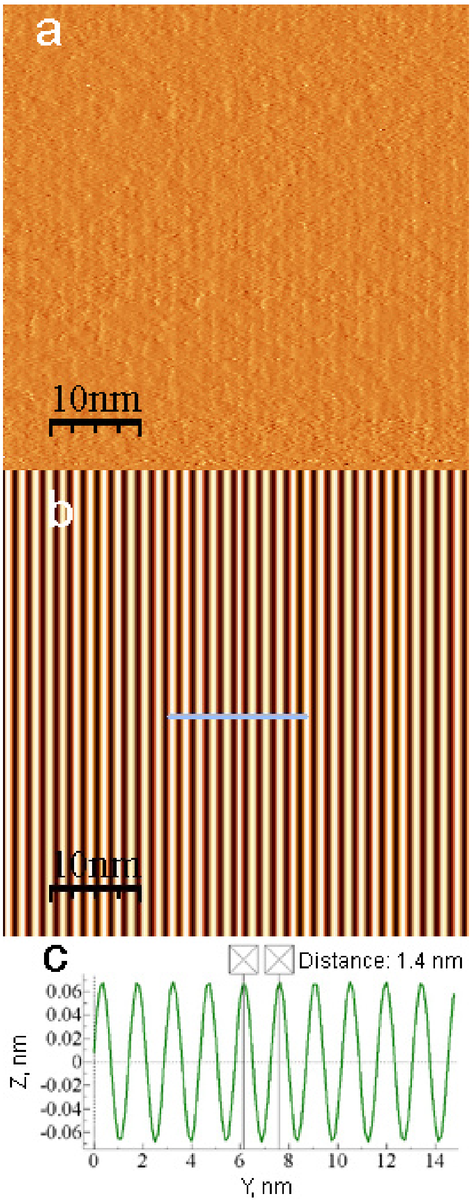

Fig. 2 STM data: (a) Constant current STM image of an In_4Se_3 (100) UHV cleavage surface 50×50 nm^2, acquired with bias voltage –1.5 V; b) Corresponding 2D FFT image with profile normal to the surface furrows; c) Periodical distance measured along the profile.

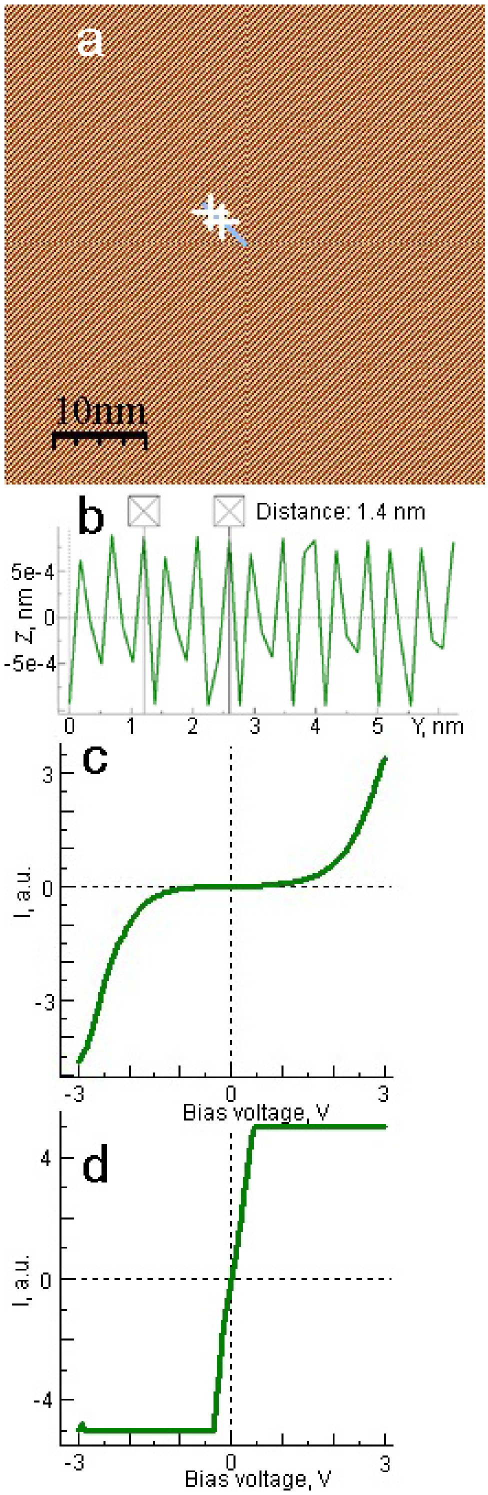

Fig. 3 STM/STS study of the In_4Se_3 (100) UHV-cleavage surface: (a) 2D FFT STM image of a 50×50 nm^2 surface area with a topography profile; (b) Subsequent profile with measured distances; (c) Typical *I–V* curve averaged over the whole studied area (spatially averaged I = f(V) curves for 110 points); (d) Local I = f(V) curve measured at an individual site, showing *I–V* behavior of a metallic-like fragment.

edges, yielding an observed value of 0.68 eV for this spectrum. The value E_g = 0.68 eV, obtained for In_4Se_3 (n-type conductivity, $n \cong 5\times10^{15}$-10^{17} cm^{-3} at 300 K) by STS, satisfactorily agrees with the values $E_g \cong$ 0.62-0.67 eV obtained for bulk In_4Se_3 layered semiconductor crystals by other experimental and theoretical methods [7,8]. In particular, this similarity correlates with the stability and the lack of reconstruction of the In_4Se_3 (100) surface structure in UHV.

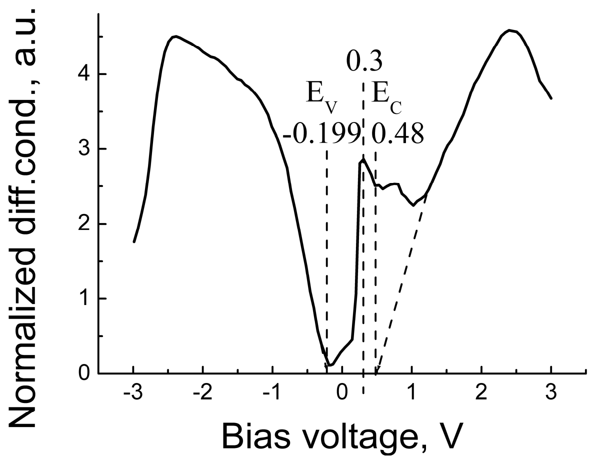

Fig. 4 Typical spatially averaged normalized STS spectrum (d(I[a.u.])/d(V[V]) / (I[a.u.]/V[V]) = f(V)) of an *n*-type In_4Se_3 (100) UHV cleavage surface, acquired from a 50×50 nm^2 area. The conduction and valence band edges are indicated by lines, and the tic mark at +0.3 V indicates a feature in the band gap region that arises from localized states.

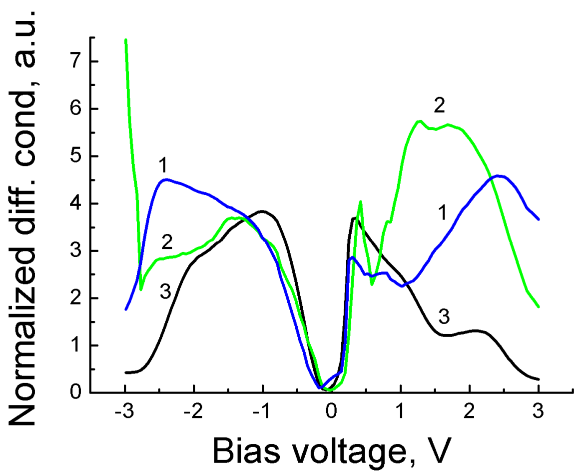

Fig. 5 STS spectra of *n*-type In_4Se_3 (100), averaged over a 50×50 nm^2 area and normalized, of UHV (1), fresh (2) and old (3) cleavages.

The tic mark at +0.3 V indicates a pronounced feature in the band gap region. Consequently, the normalized conductance is finite at the bias between the band gap edges, indicating a finite density of in-gap states. We assume that this maximum at in-gap conductance is due to overstoichiometric indium ionized impurity states, so-called localized states. This becomes obvious when analyzing the STS spectra acquired at some local points on the surface (see Fig. 3b). Besides, conduction and optical absorption experiments [9] have shown that for In_4Se_3 *n*-type layered crystals, so-called low compensated samples, the donor levels lie 0.17-0.18 eV below the conduction band.

Taking into account previous In_4Se_3 studies on (100) cleavages performed in different experimental environments by Auger electron spectroscopy, X-ray photoelectron spectroscopy, or AFM, in particular, in UHV and *ex situ* just before insertion into the UHV chamber (fresh), and also exposed for a prolonged time (old), it seemed of interest to analyze the corresponding STS spectra. Fig. 5 shows normalized STS spectra averaged over a 50×50 nm^2 area of UHV, fresh and old cleavages of In_4Se_3 (100). Despite the fact that *ex situ* cleavage surfaces of In_4Se_3 have adsorbate coverage, the DOS in the valence and conduction bands changes drastically. It is well known [10] that the valence band of In_4Se_3 is mostly formed by Se *p* electrons; the conduction band is mainly *p*-like with both In and Se contributions and sharp peaks in the DOS due to In *s* orbitals near the bottom of the conduction band. Calculations of states quantity show a clear decrease of the number of filled states in the valence band in the sequence UHV–fresh–old cleavage. Simultaneously, the quantity of empty states rises for the fresh cleavage, with respect to the UHV one, but decreases for the old cleavage. However, taking into account the rather uncontrolled conditions of the *ex situ* cleavage, it is difficult to conclude on a specific mechanism for the electron density redistribution. But in all cases, an energy gap corresponding to the In_4Se_3 gap is clearly observed.

Conclusions

We employed STM to obtain the lattice resolution of the cleavage surfaces of layered semiconductor crystals In_4Se_3 (100), and the STS method to study the local electron-energy surface structure and qualitative characteristics of the local density of states.

The cleavages obtained in UHV and in air just before placing them into the UHV chamber revealed periodic furrowed structures comparable with the bulk lattice constants. The STM results also confirm that the furrowed and chainlike surface structure of In_4Se_3 (100) UHV cleavages is stable and unreconstructed under the cleavage and exposure to UHV and might be used as an anisotropic matrix/template with low conductivity for the fabrication of surface conductive nanowires or nanostructures.

The STM/STS results show local energetic and phase inhomogeneities of the In_4Se_3 (100) cleavage surfaces on the atomic scale. The LDOS and band gap for In_4Se_3 (100) obtained by STS give the same value of the spatially averaged gap as known for bulk crystals.

A redistribution of the DOS in the valence and conduction bands of *in situ* and *ex situ* In_4Se_3 cleavages is observed in the STS spectra.

References

[1] U. Schwarz, H. Hillebrecht, H.J. Deiseroth, R. Walther, *Z. Kristallogr.* 210 (1995) 342-347.
[2] Ya.B. Losovyj, L. Makinistian, E.A. Albanesi, A.G. Petukhov, *J. Appl. Phys.* 104 (2008) 083713.
[3] P.V. Galiy, T.M. Nenchuk, Ya.B. Losovyj, Ya.M. Fiyala, *Funct. Mater.* 15 (2008) 68-73.
[4] J.-S. Rhyee, K.H. Lee, S.M. Lee, E. Cho, S.I. Kim, E. Lee, Y.S. Kwon, J.H. Shim, G. Kotliar, *Nature* 459 (2009) 965-968.
[5] I. Horcas, R. Fernandez, J.M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, A.M. Baro, *Rev. Sci. Instrum.* 78 (2007) 013705-013708 (WSxM©; http://www.nanotec.es).
[6] P.V. Galiy, T.M. Nenchuk, O.R. Dveriy, A. Ciszewski, *Phys. E* 41 (2009) 465-469.
[7] D.M. Bercha, L.Yu. Kharkhalis, A.I. Bercha, M. Sznajder, *Phys. Status Solidi B* 203 (2) (1997) 427-440.
[8] M. Sznajder, K.Z. Rushchanskii, L.Yu. Kharkhalis, D.M. Bercha, *Phys. Status Solidi B* 243 (3) (2006) 592-609.
[9] L.S. Demkiv, T.M. Demkiv, V.P. Savchyn, J.M. Stakhira, *Journal of Physical Studies* 2(4) (1998) 536-540.
[10] L. Makinistian, E.A. Albanesi, N.V. Gonzalez Lemus, A.G. Petukhov, D. Schmidt, E. Schubert, M. Schubert, Ya.B. Losovyj, P. Galiy, P. Dowben, *Phys. Rev. B* 81 (2010) 075217:1-8.

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