Structural Aspect of Formation of a Nanosystem of In/In₄Se₃ (100)

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Self-assembled indium deposition-induced nanostructures are obtained on the UHV cleaved (100) surface of In_4Se_3 layered semiconductor crystals. The small indium-deposition rates and short deposition times are chosen to study growth orientation and origin of nanostructures observed by scanning tunnelling microscopy (STM) on the (100) surface of In_4Se_3 after indium deposition. The shape of these nanostructures strictly depends on the overstoichiometric indium concentration level in the melt during the crystal growth varying from 3D islands for low concentration to elongated shapes, *i.e.*, nanowires, in the case of highly-indium-doped crystals. High-resolution STM study determines the self-assembled quasi-periodical nanowires' growth along c-axis of (100)In_4Se_3 substrate. The spatially resolved scanning tunnelling spectroscopy (STS) study revealed metallic nature of the surface of nanostructures grown on the semiconductor substrate. The growth mechanism of indium-deposited nanostructures is considered to be powered by anisotropic striated lattice structure of In_4Se_3 (100) surface with indium nuclei

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in concentration depending on the degree of overstoichiometric crystal-growth indium subsequently intercalated into the interlayer gap.

Key words: layered trichalcogenides, self-assembling nanostructures, nanowires, scanning tunnelling microscopy, scanning tunnelling spectroscopy.

Самоорганізовані індійові наноструктури одержано на надвисоковакуумній поверхні сколювання (100) напівпровідникового шаруватого кристалу In_4Se_3. Невеликі швидкості та тривалості напорошення індію вибиралися з метою дослідження ростової орієнтації та природи наноструктур на поверхні (100)In_4Se_3, які вивчали за допомогою сканувальної тунельної мікроскопії (СТМ). Форма цих наноструктур безпосередньо залежить від концентрації надстехіометричного індію в розтопі під час вирощування кристалу, змінюючись від тривимірних острівців за низької концентрації до лінійних форм, тобто нанодротів, у випадку сильно леґованих індієм кристалів. СТМ з високим розріженням уможливлює встановити, що квазиперіодичні нанодроти ростуть вздовж осі *c* кристалу In_4Se_3 на поверхні (100). За допомогою сканувальної тунельної спектроскопії з просторовим розріженням встановлено металічну природу поверхневих наноструктур на напівпровідниковій підкладинці. Встановлено, що механізм росту напорошених наноструктур зумовлений борознистою структурою ґратниці на поверхні (100) кристалу In_4Se_3 з наявністю у ній зародків індію у концентрації, яка залежить від кількости надстехіометричного ростового індію, що інтеркалюється у міжшарову щілину.

Ключові слова: шаруваті трихалькогеніди, самоорганізовані наноструктури, нанодроти, сканувальна тунельна мікроскопія, сканувальна тунельна спектроскопія.

Самоорганизованные индиевые наноструктуры получены на сверхвысоковакуумной поверхности скалывания (100) полупроводникового слоистого кристалла In_4Se_3. Небольшие скорости и длительности напыления индия использовались с целью исследования ростовой ориентации и природы наноструктур на поверхности (100)In_4Se_3, которые изучались с помощью сканирующей туннельной микроскопии (СТМ). Форма этих наноструктур непосредственно зависит от концентрации сверхстехиометрического индия в расплаве во время роста кристалла, изменяясь от трёхмерных островков при низкой концентрации до линейных форм, т.е. нанопроводов, в случае сильно легированных индием кристаллов. СТМ з высоким разрешением позволяет установить, что квазипериодические нанопровода растут вдоль оси *c* кристалла In_4Se_3 на поверхности (100). С помощью сканирующей туннельной спектроскопии с пространственным разрешением установлена металлическая природа поверхностных наноструктур на полупроводниковой подкладке. Установлено, что механизм роста напылённых наноструктур обусловлен бороздчатой структурой решётки на поверхности (100) кристалла In_4Se_3 с наличием в ней зародышей индия в концентрации, зависящей от количества сверхстехиометрического ростового индия, который интеркалируется в межслоевую щель.

Ключевые слова: слоистые трихалькогениды, самоорганизованные наноструктуры, нанопровода, сканирующая туннельная микроскопия, скани-

рующая туннельная спектроскопия.

1. INTRODUCTION

The study of self-organized structures that are formed when metal is deposited on the surface of layered compounds is interesting due to the quasi-dimensional nature of the substrate, which provides their unique electronic properties. It is well known that the electronic properties of the layered crystals can be controllable modified by the intercalation of different types of 'guest impurities' into the interlayer space [1], *e.g.*, the presence of induced nanophases on (100) surfaces of In$_4$Se$_3$ crystals specially intercalated with copper during the growth of crystals was reported [2]. Template directed self-assembly approaches are important component of the successful fabrication of nanostructures, given the long history of such studies [3]. Considering intrinsic bulk anisotropy of In$_4$Se$_3$ crystals that allows obtaining cleavages with the chainlike-furrowed structures on the nanoscale, the surface of these crystals can be used as a natural topographical template for nanosystems self-assembling. In this work, we focused on the STM/STS study to show the possibility of using (100) surfaces of In$_4$Se$_3$ crystals as tuneable interfaces for formation of deposited indium metallic nanostructures.

2. EXPERIMENTAL

The In$_4$Se$_3$ crystals were grown by the Czochralski method from the In$_4$Se$_3$ melt with wide range of overstoichiometric indium, up to 10 atomic percent (In$_4$Se$_3$ + ≤ In 10 at.%). Thus, obtained crystals were *n*-doped by In with a carrier concentration of $10^{15}/10^{19}$ cm^{-3} (as measured at 0.01/0.11 (Ohm·cm)$^{-1}$, the low/high conductivity, respectively). Samples for STM/STS studies had special 3×4×6 mm^3 shape for cleavage *in situ*. Thus, the several cleavages could be obtained for structurally perfect samples in UHV. The crystals were thermotreated *in situ* after growth during 12 hours as well as after indium deposition (0.5 hour) at fixed temperatures up to 600 K.

  The STM/STS data were obtained at room temperature with an Omicron NanoTechnology STM/AFM System in UHV better than 10^{-10} Torr. The constant current mode acquisition was used for STM with 400×400 data points resolution. STS was acquired in the current imaging tunnelling spectroscopy (CITS) mode with 80×80 data points resolution. Thermal evaporator EFM-3 was applied for indium deposition in UHV. Indium-ion current inside the effusion cell was maintained to

be constant during the indium deposition. The deposition rate was kept at approximately **0.01 ML/min**. Small deposition rates were chosen intentionally to produce heterogrowth, rather than obtaining of polycrystalline films at high deposition rates. Such rates allow organizing an activated-migration movement of deposited indium with localization on growth activation centres.

The representation and analysis of STM/STS data were conducted by the WSxM software v.4.0 designed by Nanotec Electronica [4].

3. RESULTS AND DISCUSSION

The (100) surface of In_4Se_3 orthorhombic layered crystals obtained due to the cleavage in UHV is a perfect natural pattern with a furrowed structure characterized by the following crystallography parameters [5]: in length located along the c axis and normal to b axis ($c = 4.08$ Å, $b = 12.3$ Å). Such a structure of the surface can be verified by means of atomic force microscopy and STM studies, which, as a rule, manage to achieve lattice resolution [6, 7]. However, for STM images, the lattice resolution without two-dimensional fast Fourier transform (2D FFT) filtration can be obtained easy for In_4Se_3 crystals grown with a greater amount of overstoichiometric indium in the melt. Taking into account the peculiarities of the STM method, this fact confirms well known intercalation process in the layered crystals, and hence, the influence of indium intercalation on the conductivity of the crystal surface, since the (100)In_4Se_3 surface in our case is a part of the interlayer gap obtained as a result of cleavage. The intercalation of interlayer gaps in layered crystals by impurity guests is common process widely studied [1].

We find that only spatially distributed In clusters or irregular three-dimensional (3D) islands are formed on (100) surface of In_4Se_3 crystal with low conductivity (or low indium overstoichiometric concentration in the melt). Figure 1, a shows typical STM image of low-conductive In_4Se_3 (100) surface after 1 min indium deposition. We can observe single different sized 3D islands located on the surface without visible signs of ordering.

Figures 1, b, c and subsequent profiles d, e demonstrate typical dimensions and time delay of feedback in the tip-surface system obviously associated with a striking change in the spatial distributed conductivity.

We conducted a detailed STS study to find out the nature of such nanostructures that arose on the surface after indium deposition. The STS allows relatively easy to distinguish between semiconductor and metallic character of them. Figure 2, a shows low-resolution STM image obtained simultaneously with STS data acquisition. However, its resolution is sufficient to locate 3D island on the surface, the same as
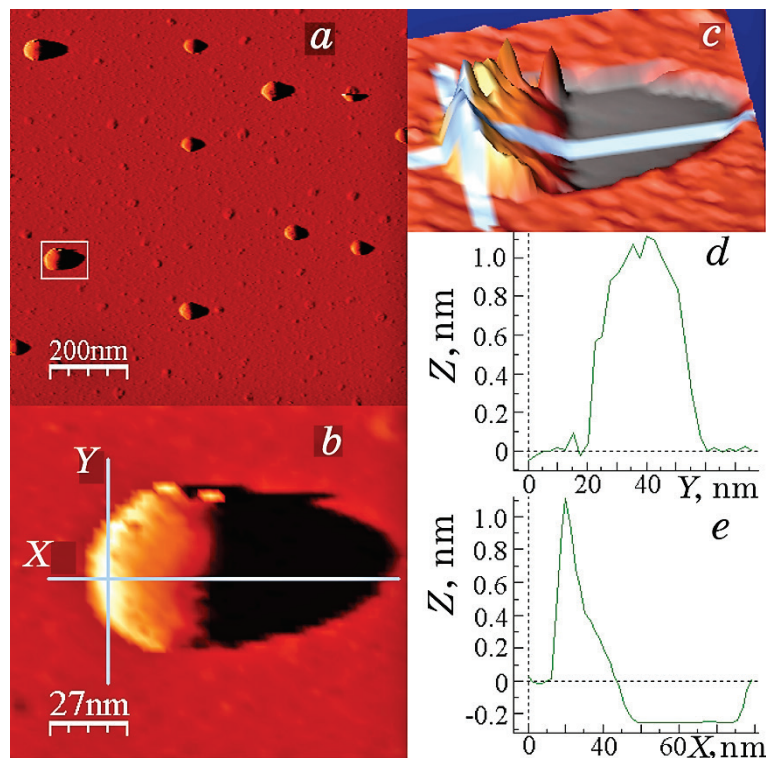
Fig. 1. STM image (*a*) of low conductive In$_4$Se$_3$ (100) surface after 1 min In deposition (1×1 µm^2 area, +2.5 V bias, 105 pA); *b*, *c*—2*D* and 3*D* images of zoomed fragment indicated in (*a*) with subsequent *Y* and *X* direction height profiles (*d*) and (*e*), consequently.

shown in Fig. 1, *a*. The tunnelling current−voltage (*I*−*V*) curves were measured in specific points of the surface shown on insets in Fig. 2, *c*, *d*. The *I*−*V* curves in Fig. 2, *c* exhibit metallic nature and we relate them with indium metallic clusters. At the same time, *I*−*V* curves presented in Fig. 2, *d* have strictly semiconductor character with band gap that is consistent with that of In$_4$Se$_3$ bulk [8]. Therefore, we can deduce that shapes formed on semiconductor (100) surface of In$_4$Se$_3$ are indium deposits.

Elongated indium nanostructures begin to form on the surface of In$_4$Se$_3$ crystals with high conductivity. Figure 3, *a* shows typical STM image of high conductive In$_4$Se$_3$ (100) surface with indium nanostructures that are obtained under comparative conditions of indium deposition and subsequent annealing as for that presented in Fig. 1, *a*. The indium nanostructures shown in Fig. 3, *a* have a large length/width ratio confirmed by subsequent profiles presented in Figs. 3, *b* and *c*.

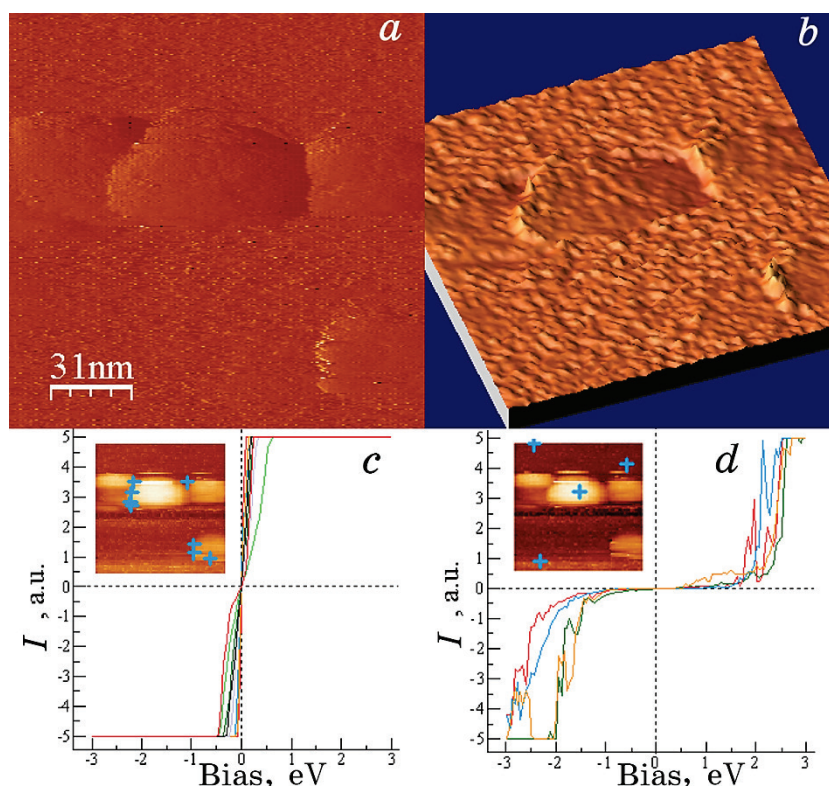Comparing typical indium nanostructures shown in Fig. 1, *a* and

Fig. 2. STM/STS study of In—In$_4$Se$_3$ system: *a*, *b*—2*D* and 3*D* low resolution STM images obtained simultaneously with STS data acquisition (154.7×154.7 nm^2 area); *c*, *d*—current voltage curves obtained at specific points indicated in the corresponding insets.

Fig. 3, *a*, one can conclude that their formation is influenced by the growth characteristics of In$_4$Se$_3$ crystal, and thus, properties of subsequent cleavage's (100) surface as template. In fact, the crystals and their surfaces act as a tuneable interface for obtaining the special shaped nanostructures.

In order to determine the orientation of such elongated nanostructures, we examined randomly chosen sufficiently small 60×60 nm^2 size area (see Fig. 3, *d*) within the 1×1 μm^2 STM image shown in Fig. 3, *a*. The rescanned small size image allowed to obtain higher spatial resolution sufficient to withdraw lattice resolution typical for In$_4$Se$_3$ (100) surface. Figure 3, *d* allows determining *b* and *c* axes directions that are undoubtedly visible on the surface. Moreover, the results of 2*D* FFT filtration presented in Fig. 3, *e* with subsequent periodical profile in Fig. 3, *f* revealing characteristic $\cong$ 1.2 nm size along *b* axis indicate that elongated indium nanostructures on (100)In$_4$Se$_3$ surface are ori-
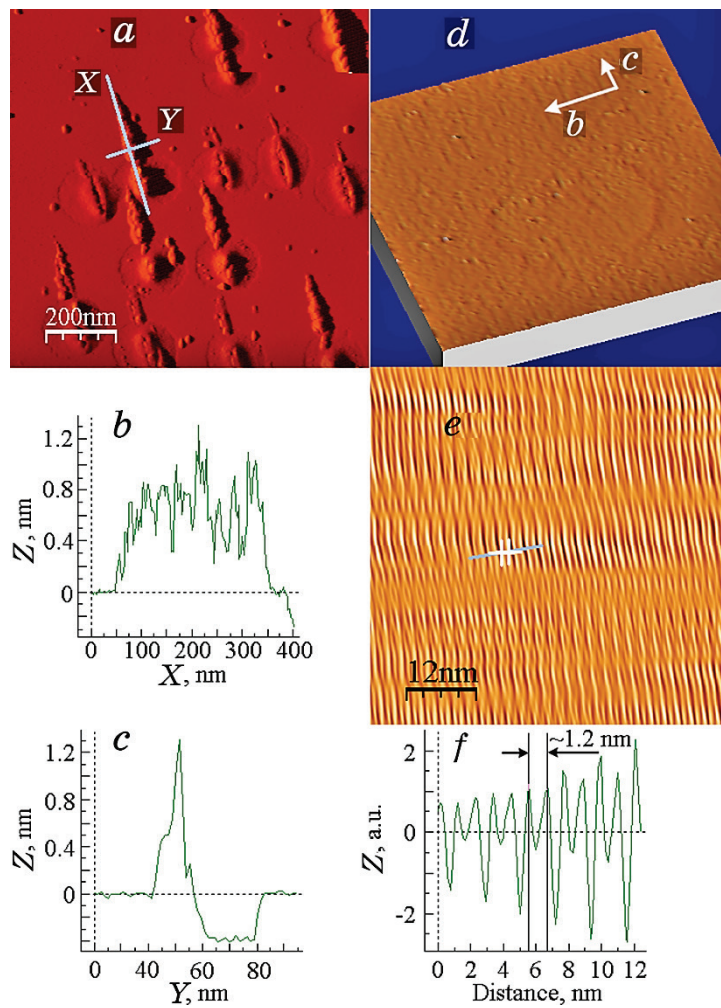
Fig. 3. STM image (*a*) of high-conductive In$_4$Se$_3$ (100) surface after 1 min In deposition (1×1 μm^2 area, +1.6 V bias, 86 pA) with subsequent height profiles *b* and *c*; 3*D* STM image (*d*) of rescanned randomly 60×60 nm^2 area chosen in Fig. 3, *a* (+1.6 V bias, 86 pA) showing *b* and *c* growth directions of indium nanostructures and corresponding 2*D* FFT image (*e*) with subsequent height profile (*f*).

ented along **c** axis, *i.e.*, along the striated surface relief.

It is well known [5, 9] that crystal structure of In$_4$Se$_3$ is dominated by multivalent clusters of indium atoms in positions In1, In2, In3, *i.e.*, (In3)$^{5+}$ bonded with selenium in the layer-packet (see Fig. 4, *a*) and elevated In atoms in position In4 (In$^+$ ions), which are very weakly connected to the rest of the atoms and form an infinite one-dimensional

chain along c-axis direction [001]. The In^+ atoms 'go out' to the surface, when the crystal is cleaved (see Fig. 4, a), along the interlayer plane (normal to a-axis) and, thus, take part in the nucleation of deposited In atoms.

The orientation effect of the substrate on the heteroepitaxial growth of indium-deposited nanostructures is determined not so much by force as by the structural-geometric features of atomic rough $(100)In_4Se_3$ cleavages. The oriented nuclei might arose out of the location of the potential wells on the cleavage surfaces and the activation rows of the indium ions In^+, on which precipitating In atoms are located with a minimum of energy and, as a result, one could observe the
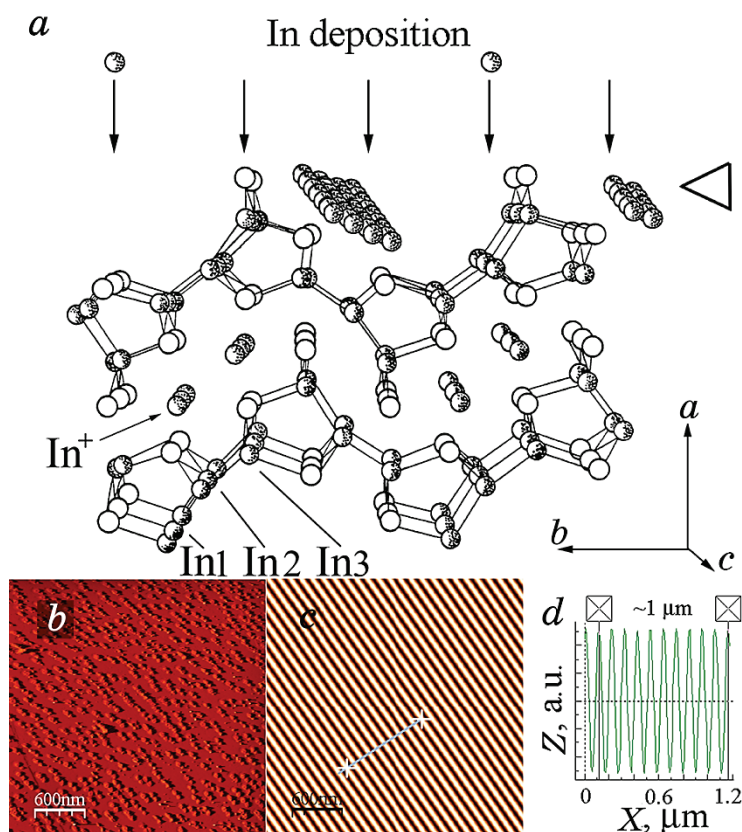

Fig. 4. Model image of the heteroepitaxial growth of the indium coverage on indium nuclei atoms which are present on the $(100)In_4Se_3$ cleavage surface: fragment of the layered structure of the crystal (projection onto the (001) plane), which shows In^+ atoms that 'go out' to the surface; the triangle indicates the direction of the cleavage (a); b—3×3 μm^2 STM image of the indium nanodimensional structures on the $(100)In_4Se_3$ surface after 2 min In deposition (1.2 V bias, 83 pA) and its $2D$ FFT image (c) with subsequent profile (d).

orientation heteroepitaxial growth of low-dimensional indium nanostructures and indium nanosystems on the (100)In$_4$Se$_3$ surfaces of crystalline packet-layers.

Since the rows of In$^+$ atoms are present on the surface for any In$_4$Se$_3$ crystal, it remains to understand the differences in the form of deposited indium nanostructures, which vary from irregular 3D islands to quasi-periodical linear shaped structures for (100) surfaces of In$_4$Se$_3$ crystals grown from a melt with different amounts of overstoichiometric indium. We consider that shape dependence of In deposited structures on In$_4$Se$_3$ crystal growth conditions is powered by indium intercalation, namely, self-intercalation process. The In$_4$Se$_3$ peculiarity is that just indium is such impurity guest. Obviously, that part of overstoichiometric indium, which is necessary present during In$_4$Se$_3$ growth, naturally intercalates crystal. We can make an assumption, which, in our opinion, is confirmed in this work, that, depending on intercalated indium atoms' concentration, they primarily are located, like In$^+$ atoms, along the furrows on the (100) surface, thus, leading to high density of natural In nuclei when deposited In nanostructures are formed. Thus, high concentration of overstoichiometric indium in the melt is found to be favourable for the formation of nanowires than 3D islands indicating that indium 'wetting layer' due to layered crystal self-intercalation plays a dominant role in formation of deposited indium nanostructures.

Figure 4, b shows In nanostructures formed on the (100) surface of high conductive In$_4$Se$_3$ crystal after 2 min of indium deposition. These elongated structures form a quasi-periodical matrix on a large scale. Moreover, 2D FFT filtered image, shown in Fig. 4, c with subsequent profile (see Fig. 4, d) reveals a clear periodicity and direction of these nanostructured formations with a period of about 100 nm. Such a fairly large value can be justified on the basis of the Gibbs–Thomson effect, which has a major impact on nanostructures growth: at a given vapour pressure, smaller deposited indium droplets will desorb more atoms than larger ones, which will suppress the nanowire growth from droplets smaller than a certain critical radius [10].

4. CONCLUSIONS

In summary, the influence of In$_4$Se$_3$ growth conditions on shape of In deposited nanostructures on the (100)In$_4$Se$_3$ surface has been studied by STM/STS. The switching in the nature of the self-assembling of the resulting nanostructures from the 3D islands to the elongated parallel quasi-ordered nanostructures is due to the peculiarity of the growth conditions of In$_4$Se$_3$ substrate crystals with the presence of overstoichiometric indium followed by its self-intercalation. Thus, formation of indium deposited nanostructures provides ability to study

their electronic properties and peculiarities of In$_4$Se$_3$ layered crystal intercalation. Furthermore, that leads to perspectives of novel electronic devices fabrication.

ACKNOWLEDGEMENTS

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