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СТРОЕНИЕ И СВОЙСТВА НАНОРАЗМЕРНЫХ И МЕЗОСКОПИЧЕСКИХ МАТЕРИАЛОВ

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Ni$_x$InSe (0001) Metal–Semiconductor Heteronanosystem Study

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Scanning tunnelling microscopy/spectroscopy (STM/STS) data show that InSe layered crystal intercalated with nickel is a heteronanosystem—InSe layer-packet that alternates with nickel at fine dispersed phase in the interlayer gap. For analysis of the degree of metallicity of cleavage surfaces, an array of STS data obtained in the current imaging tunnelling spectroscopy (CITS) mode is used. By significantly different behaviour of current–voltage curves for metal and semiconductor at localized points of surface analysis on the cleavage within the bias voltages that correspond to the band gap of the semiconductor, the method for the calculation of the relative metal concentration on the cleavage surface is proposed. The constraints for this method of the relative concentration estimates are analysed. As determined, the value of the nickel relative concentration in the interlayer gap for the Ni$_x$InSe systems can be up to 2%, taking into account features of obtaining of the cleavage surfaces in the layered crystals. To establish the structural characteris-

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tics of the nickel, the STM analysis with high spatial resolution is used followed by the $2D$ FFT filtration and height profiling of image data. The analysis of corresponding revealed periodicities allows revealing formation of the two-dimensional square lattice of nickel on certain nanoscale areas of surface.

Key words: scanning tunnelling microscopy and spectroscopy, current imaging tunnelling spectroscopy, local density of states, layered crystals, metal intercalation, heteronanostructures.

За допомогою метод сканувальної тунельної мікроскопії та спектроскопії (СТМ/СТС) встановлено, що шаруватий кристал InSe, інтеркальований ніклем, представляє собою гетеронаносистему — шар-пакет InSe, який чергується з ніклем, що знаходиться у дрібнодисперсній фазі у міжшаровій щілині. Для аналізи ступеня «металічности» поверхні сколення використано масив даних СТС, одержаних у режимі CITS (current imaging tunnelling spectroscopy). За істотно різною поведінкою вольт-амперних кривих для металу та напівпровідника в локальних точках аналізи на поверхні відколу, одержаних у діяпазоні напруг зміщення, які відповідають забороненій зоні напівпровідника, запропоновано методу обрахунку відносних концентрацій металу на поверхні сколення. Проаналізовано обмеження такої методи оцінювання відносних концентрацій. Встановлено, що величина відносної концентрації ніклю у міжшаровій щілині для систем $\mathrm{Ni}_x\mathrm{InSe}$ може досягати близько 2%, враховуючи особливості одержання поверхонь сколення для шаруватого кристалу. Для встановлення структурних характеристик ніклю використано СТМ-аналізу з високою просторовою роздільчою здатністю з наступною $2D$-FFT-фільтрацією і висотним профілюванням одержаних зображень. Аналіза відповідних періодичностей уможливила виявити формування двовимірної квадратної ґратниці ніклю на окремих наномасштабних ділянках поверхні.

Ключові слова: сканувальна тунельна мікроскопія, сканувальна тунельна спектроскопія, локальна густина станів, шаруватий кристал, інтеркаляція металу, гетеронаноструктури.

С помощью методов сканирующей туннельной микроскопии и спектроскопии (СТМ/СТС) установлено, что слоистый кристалл InSe, интеркалированный никелем, является гетеронаносистемой — слой-пакетом InSe, который чередуется с никелем, находящимся в мелкодисперсной фазе в междуслоевой щели. С целью анализа степени «металличности» поверхности скалывания использован массив данных СТС, полученных в режиме CITS (current imaging tunnelling spectroscopy). По существенно различному поведению вольт-амперных кривых для металла и полупроводника в локальных точках анализа на поверхности скалывания, полученных в диапазоне напряжений смещения, которые соответствуют запрещённой зоне полупроводника, предложен метод расчёта относительных концентраций металла на поверхности скалывания. Проанализированы ограничения такого метода оценки относительных концентраций. Установлено, что величина относительной концентрации никеля в междуслоевой щели для систем $\mathrm{Ni}_x\mathrm{InSe}$ может достигать около 2%, учитывая особенности получения поверхностей скалывания для слоистого кристалла.

С целью установления структурных характеристик никеля использован СТМ-анализ с высоким пространственным разрешением с последующей 2*D*-FFT-фильтрацией и высотным профилированием полученных изображений. Анализ соответствующих периодичностей позволил установить формирование двухмерной квадратной решётки в отдельных наномасштабных областях поверхности.

Ключевые слова: сканирующая туннельная микроскопия, сканирующая туннельная спектроскопия, локальная плотность состояний, слоистый кристалл, интеркаляция металла, гетеронаноструктуры.

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1. INTRODUCTION

One of the notable features for the semiconductor-layered crystals, which include InSe, is the presence of Van der Waals interlayer gap, allowed to introduce here the outer atoms such as, 3*d*-atoms of iron group metals, including nickel, chromium by process of intercalation. Thus, obtained hybrid InSe (Me) structures are a system of ‘flat’ nanostructures formed by magnetic impurities of 3*d*-metal atoms [1]. Hybrid metal-layered semiconductor nanosystems are attracting the great interest considering their perspective to be the base of novel nanosize devices. The study of hybrid systems by scanning tunnelling microscopy/spectroscopy (STM/STS) methods is relevant in terms of forming a microscopic basis for the creation of such nanoscale devices [2]. The valuable nanoscale properties of Ni_xInSe hybrid metal–semiconductor system studied in this paper are due to the relatively easy way of its obtaining as self-assembling system. This paper aims at analysis of nickel occurrences in the interlayer gap and the evaluation of relative metal concentration in it.

2. EXPERIMENTAL

Ni_xInSe layered intercalate crystals have been grown by Bridgman–Stockbarger method from previously synthesized melts InSe + x at.% Ni ($x \leq 10\%$). The synthesis was carried out for three days at a temperature below 960°C to prevent the formation of nickel selenides’ compounds. The grown Ni_xInSe layered crystals were thermo-treated during 60 hours for better thermodynamic equilibrium nickel intercalation [3, 4]. STM/STS data were obtained by Omicron Nano Technology STM/AFM System operating with UHV better than 10^{-10} Torr at room temperature. The nickel-intercalated samples were cleaved by stainless tip *in situ* and just obtained (0001) surface plane was studied by STM/STS.

The acquisition of STM data was conducted in the constant current mode. For STS studies, we used current imaging tunnelling spectroscopy (CITS) mode. Free software WS&M v.4.0 from Nanotec Electronica [5] was used while analysing and processing of STM/STS data.

3. RESULTS AND DISCUSSION

The experimental research objects, such as InSe and their Ni_xInSe intercalates have the layered structure and their (0001) surface might be just get easily by cleavage even in UHV. Since the crystals are easily cleaved along the Van der Waals interlayer gaps, the STM/STS studies in addition to the only surface properties, what is obvious, provide an opportunity to consider what is in the bulk of crystal because we physically examine the contents of the interlayer gap. STS study in CITS mode is often used for analysis of spatial and electronic variability of layered semiconductors with presence of a large concentration of defects and impurities [6]. CITS mode allows to obtain matrix of experimental data, including, current–voltage ($I-V$) curves discretized over bias voltage which are associated with local points ($\cong$1 Å) of analysis on the surface (6400 points). Thus, 6400 $I-V$ curves over the studied area have 1/80 X (size dimension) × 1/80 Y (size dimension) spatial distribution (80×80 pixel matrix size). So, resolution is only affected by choice of studied area size. Using $I-V$ curves allows to evaluate the detailed local surface electron energy structure, since dI/dV value as a function of probing tip—(0001) sample surface bias voltage ($dI/dV = f(V)$) is proportional to the local density of states (LDOS). CITS-mode also combines spectroscopy analysis with presentation of corresponding STM images. The STM image is actually a reflection of the surface density of states at local points and the probe tungsten tip one convolution at a certain value of bias voltage. However, it should be noted that STM images obtained simultaneously during the STS data acquisition have a significantly lower resolution, than ones acquired in STM mode (400×400 pixel matrix size), but they allow to identify clearly the nature metal or semiconductor one of the topographic inhomogeneities presented on the appropriate STM image.

Figure 1, *a* shows three-dimensional (3*D*) STM image obtained as described above during STS data acquisition. We intentionally applied the derivative filter to STM image with the aim of amplifying of the surface inhomogeneities' visual representation. Figure 1, *a* shows the relatively smooth selected area labelled as 1. The appropriate $I-V$ and normalized derivative dI/dV curves for this area are presented on Figs. 1, *b*, *c*. They have the typical semiconductor nature with a band gap value of 1.4 eV, which is characteristic for InSe crystal. Zero values of tunnelling current in the vicinity of zero bias voltage probing the range between the top of valence band E_v and the bottom of conduction band E_c are related with lack of LDOS at the energy gap E_g of semi-

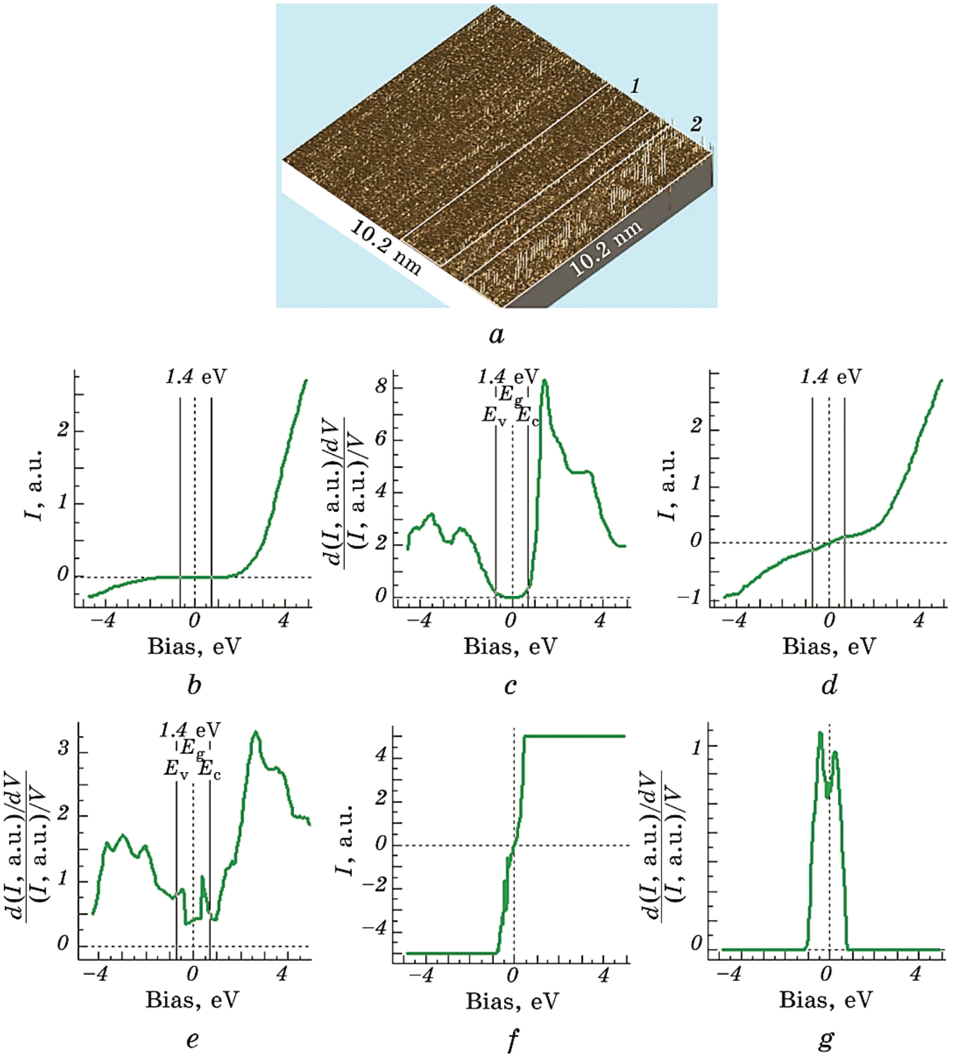


Fig. 1. STM/STS study of Ni$_x$InSe hybrid metal–semiconductor system: 3*D* STM image with 10.2×10.2 nm^2 size obtained simultaneously in STS mode, 4.2 V bias, filter derivative (*a*). I–V and normalized derivative dI/dV curves acquired from the selected area (*1*) on Fig. 1, *a* (*b*, *c*). I–V and normalized derivative dI/dV curves acquired from the selected area (*2*) on Fig. 1, *a* (*d*, *e*). I–V and normalized derivative dI/dV curves acquired from the local Ni cluster (*f*, *g*).

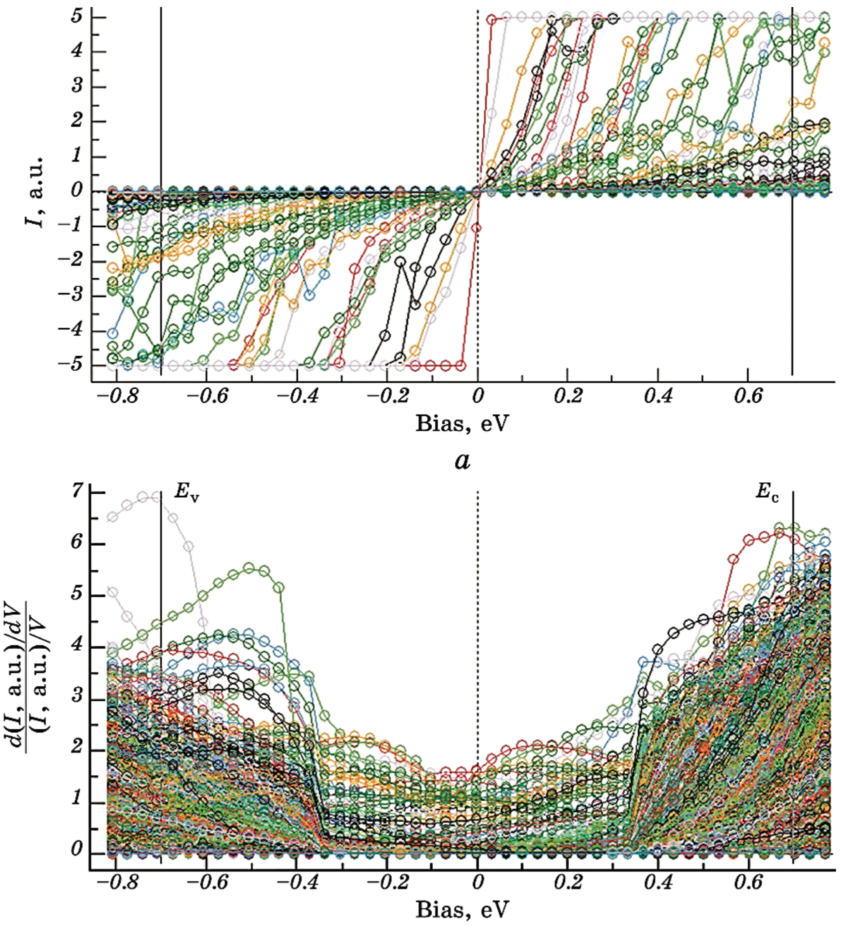
conductor involved into the tunnelling process: at negative bias—from the sample to the tip and *vice versa* at positive one.

However, another selected area on the surface labelled as 2, which is not smooth, reveals somewhat different behaviour of these curves with a nonzero value of tunnelling current within the range of bias corresponding to the energy gap of InSe (see Figs. 1, *d*, *e*). Observed changes in curves' behaviour in the vicinity of zero bias are influenced by significant amount of localized states, which are due to Ni available on selected area. The most revealing from the viewpoint of the presence of localized states associated with Ni intercalate are data on Figs. 1, *f*, *g*, that show *I–V* and normalized derivative *dI*/*dV* curves acquired locally at a single point of analysis just over the metallic cluster. In this case, branches of *I–V* curve on Fig. 1, *f* show almost linear dependence of tunnelling current *versus* tip–sample voltage bias what is true for tunnel junction metal (probing tip)–metal (sample surface). Normalized derivative *dI*/*dV* curve on Fig. 1, *g* shows high density of states in the vicinity of Fermi level.

Thus, the use of STS for the analysis of metal intercalate availability, determining its location on the surface of the cleavage and, consequently, in the interlayer gap is based on significantly different behaviour of the current–voltage characteristics for the metal and the semiconductor in a range of bias voltages corresponding to the energy band gap of semiconductor [7].

On the basis of above considerations, we have proposed a method for estimating the presence of dispersed phase metal clusters on the surface of the semiconductor due to intercalation process with the ability to evaluate concentration of metal on the surface and spatial visualization of the studied area. The presence of intercalated metal on the surface can be easily detected by the availability of the tunnelling current above a certain 'background values' that occurs in bias voltage range that allows probing energy gap of semiconductor. The choice of 'background values' of tunnelling current due to ΔV bias corresponding to the value of forbidden energy band, above which a given analysis local point on the surface could be classified as 'metallicity class', can also be affected by the quality of the cleavage surface. In particular, for surface of layered crystals such as (0001) Ni_xInSe, the stairs obtained after cleavage may also lead to the appearance of localized states in the band gap of the semiconductor.

Figures 2, *a*, *b* show sets of *I–V* curves acquired at tungsten tip - (0001) Ni_xInSe surface system and their differentiated and normalized representation (*b*) obtained by the CITS method for the array of 6400 analysis points spatially distributed on 10×10 nm^2 surface area. Circles on the curves show discrete corresponding experimental values obtained at, so-called, ramp points each biased by 0.035 V step. In fact, in the analysis of experimental *I–V* curves' array, we are dealing with three-dimensional data matrix where each pair of columns' values bias voltage–tunnelling current is localized to a specific point on the surface. Discreteness of these points in the sub nanoscale along the successive scans on the surface depends on the size of the analysed area selected for scanning with the standard number of counts, as men-



a

b

Fig. 2. The typical sets of 6400 *I*–*V* (*a*) and normalized derivative *dI*/*dV* (*b*) curves, respectively, acquired from 10×10 nm^2 size area of Ni$_x$InSe hybrid metal–semiconductor system with bias values limited by 1.4 eV InSe energy gap. Circles on the curves show discrete corresponding experimental values.

tioned above. Thus, for 10×10 nm^2 surface studied area of the sample, each vectors' pair of tunnelling current–bias voltage in the array of local *I*–*V* experimental data is obtained with discreteness of 1.25 Å.

This choice of the analysed area size helps to be ensured that the entire spatial area is covered by the STS analysis, since it is known that the point tunnel contact (current) probes area with diameter of ≅ 1–2 Å, in particular, sensing depends on the quality of tungsten tip that finally determines its atomic resolution at a point of tunnel contact. Therefore, the obtained ratio of the *I*–*V* curves 'metal' to 'semiconductor' ones in subnanoscale for (0001) Ni$_x$InSe heteronanosystem allows to estimate the percentage concentration of nickel.

Such analysis can be easily carried out using the **FREQUENCY** function for statistics analysis build-in the spreadsheet dealing with two parameters—data set and intervals (data set—part of experimental

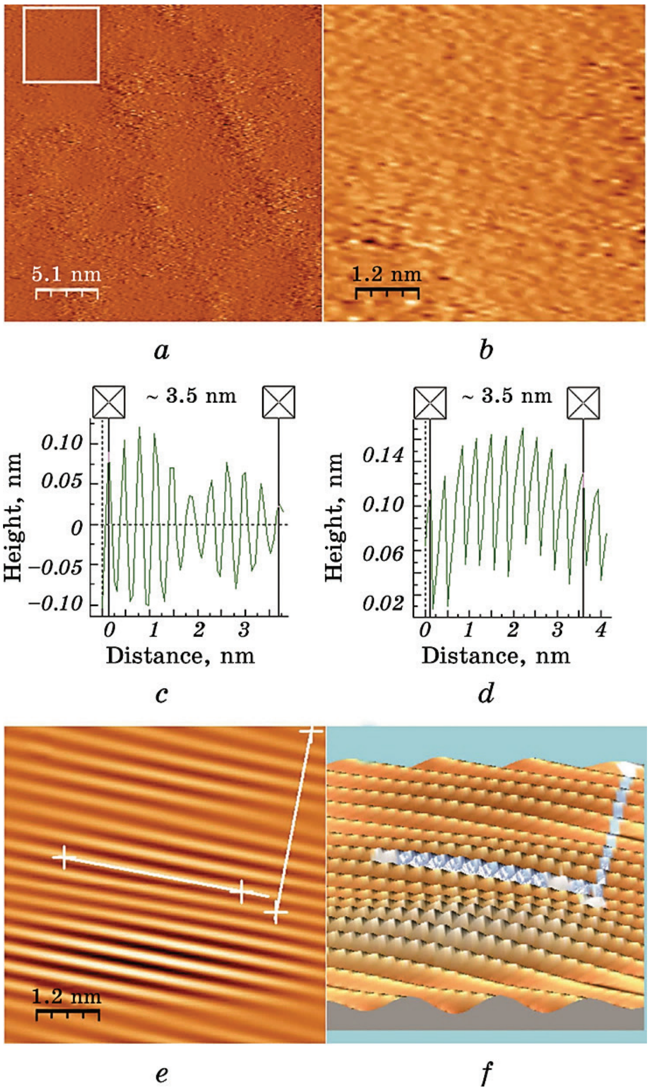


Fig. 3. STM mode study of Ni$_x$InSe hybrid metal–semiconductor system: 25.7×25.7 nm^2 image acquired at +4.6 V bias, 103 pA constant tunnelling current (*a*). 6.2×6.2 nm^2 zoomed in smooth area marked by white square on (*a*) (*b*). Height profiles obtained respectively normally to and along the visible periodicities on an image (*e*) (*c*, *d*). 2*D* and 3*D* images obtained due to 2*D* FFT-filtering of (*b*) with corresponding marked profile directions (*e*, *f*).

data matrix with tunnelling currents within the voltage bias range corresponding to the band gap of InSe ($E_g = 1.4$ eV); intervals—level of 'tunnelling current value background' in band gap semiconductor bias range, above which a given point of analysis includes to 'metallicity class'. For a small sample size of STS data from various 10×10 nm^2 areas on the surface, this value was averaged as $\cong$1% fluctuating in 0.8–1.25% range for different ones.

Apparently, it is worth to analyse the correctness of received values of relative nickel concentrations or, in generally, intercalated metal, on the surface of the layered semiconductor crystal using our proposed method.

Nickel on the surface of the cleavage is really just only a 'part of the whole' remaining and analysed by STS relative to the other, which is removed in a result of cleavage. Therefore, the average estimate of metal concentration may be doubled. As mentioned above, it is also an important the selection of spatial probe step, which is due to the size of the selected area of STS analysis, given the locality of $\cong$1–2 Å of the tunnelling current collection diameter. It is necessary for complete overlapping of the studied area by STS analysis. Although, in this case, nickel concentrations' estimates obtained for many areas of STS analysis and averaged over sufficiently large areas of the surface in nanoscale can somewhat vary from those achieved by other methods such as x-ray photoelectron spectroscopy, which 'integrates' experimental data on a macroscale [1]. It is clear that the reliability of relative concentrations of nickel calculations on the surface also depends on the thickness of its layer. In the case that dispersed metal phase does not exceed height of nickel monolayer, the above evaluation method is valid, otherwise the further analysis is required. The crystal structure of layered crystals InSe, where the distance between layers of 3.08 Å [8], that is comparable with the doubled atomic radius of nickel [9], suggests that nickel clusters are distributed on the surface with the height that does not exceed a monolayer.

With these reservations, it could be concluded that the proposed model is appropriate for calculating of the relative concentrations of dispersed metal phase on the (0001) surface of Ni_xInSe heteronanosystem and their like ones on the base of the density of surface electronic states STS study.

However, besides the presence of metal intercalate on the surface, it is also important to establish ones structural characteristics. This can be applied using a separate STM study with a high resolution as mentioned above for areas on the surface previously classified using STS as coated by metal. Figure 3 shows STM results obtained on smooth studied area marked by white square on (*a*) filtered by 2*D* Fast Fourier Transform (FTT) conversion (*e*) that allowed to recognize distinct two-dimensional surface structure characterized by surface square lattice with vectors roughly equal to 3.5 Å derived from the subsequent profiles (*c*, *d*). Figure 3, *f* shows corresponding 3*D* presentation of filtered image. Such a lattice, cubic close packed one with appropriate lattice parameters' values, as known, is inherent to nickel [9]. Thus, in a result of STM study, we were able to establish that nickel forms its own phase being introduced into the interlayer gap in a result of InSe crystal intercalation.

4. CONCLUSIONS

The results of STS/STM studies established the presence of localized surface states in electron-energy structure of the (0001) cleavage surface of Ni_xInSe heteronanosystem due to fine phase of nickel metal clusters distributed in the interlayer gap of InSe layered crystal.

We have proposed model for calculation of relative concentrations of dispersed metal phase on the (0001) surface of Ni_xInSe and the like ones intercalated metal–layered semiconductor based on acquired experimental STS data on the localization of density of surface electronic states.

The averaged (in the nanoscale size) estimate of the metallicity degree of (0001) cleavage surface of InSe layered semiconductor crystal intercalated by nickel might be carried out at approximately 2% level, given the fact that such surface is obtained in a result of cleavage.

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