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Photoelectric properties of In_2O_3 -InSe heterostructure with nanostructured oxide

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Abstract. The photosensitive In_2O_3 -*p*-InSe heterostructures, in which the In_2O_3 frontal layer has a nanostructured surface, have been investigated. The photoresponse spectra of these heterostructures have been found as essentially dependent on surface topology of oxide. The obtained results indicate that In_2O_3 oxide is not only an active component of the structure but also acts as a diffraction cell element. Oxide surface topology was investigated using the atomic-force microscope technique. Under different conditions of InSe oxidation, the sample surfaces contained nanoformations preferably in the form of nano-islands. Their location acquired both disordered and ordered characters. A dimensional optical effect in the oxide layer was found to be due to the anisotropic light absorption in InSe. The higher deviation of incident light from its normal direction due to a nanostructured surface is, the higher variation in generation of carriers in this semiconductor is. These changes consist in the energy broadening of the heterostructure photoresponse spectrum as well as in peculiarities of the excitonic line. The higher density and ordering of the nanoneedles on the oxide surface is, the higher long-wave shift and more intense excitonic peak in spectrum takes place.

Keywords: InSe, In_2O_3 , heterostructure, photoelectric properties, atomic-force microscopy, nanostructured surface.

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1. Introduction

The phenomena of diffraction and interference of light are commonly observed using a diffraction grating or network. These devices have a periodic structure of grooves or cells with the sizes comparable to the wavelength of light. It is of some interest to study interaction of light with materials that have a nanostructured surface. The surface nanoobjects can have a different topology (shape, size) and their ordering. Since the nanoobject sizes are by an order of magnitude smaller than, for example, the grating constant is, the nanostructured surfaces have to possess the strong diffraction properties.

A surface nanostructured relief can be obtained, in particular, by formation of the heterostructures [1, 2]. The growth of a heterostructure frontal layer is usually accompanied with formation of nanostructured objects on its surface. Varying the growing conditions for this layer, one can influence the structure of the surface relief. The frontal layer of the photosensitive

heterostructure also serves as its wide-band-gap window. At normal incidence of light on the transparent nanostructured surface and when the dimensional optical effect (diffraction) to be occurred, it will take place a deviation of light from its initial direction. Using the anisotropic crystals as semiconductor substrates, one can expect that the photoelectric properties of heterostructures will be determined by degree of light diffraction.

InSe, GaSe layered crystals serve as examples of semiconductor substrates with the strongly anisotropic properties. They are used in many heterostructures due to the possibility of making the high-quality substrates by cleaving the crystal [3]. The In_2O_3 -InSe structure is one of these heterostructures in which the oxide film is obtained by thermal oxidation of InSe [4]. The photoresponse spectra of the In_2O_3 -InSe heterostructures are essentially different for the $\mathbf{E}\perp\mathbf{c}$ and $\mathbf{E}\parallel\mathbf{c}$ orientations of the incident light polarization, where \mathbf{E} is the electric-field vector of the electromagnetic wave; \mathbf{c} is a crystallographic axis which is also perpendicular to the

cleavage plane [5]. The use of such heterostructures serves as an ideal model for detecting the dimensional optical effects provided that the oxide surface is nanostructured and the substrate is anisotropic.

The nanoanalysis of InSe surface topology by using the atomic force microscope (AFM) images confirmed the formation of nanoobjects on the surface of the as-cleaved crystals [6], on the surface of the samples subjected to the influence of the AFM probe [6, 7], and on the surface of intrinsic oxides of these crystals [8]. The aim of the present article is an experimental investigation of diffraction properties inherent to the nanostructured surface in In₂O₃-InSe heterostructures.

2. Experimental

InSe(Cd) crystals were used for our investigations. They were grown from a nonstoichiometric melt of the InSe composition by using the Bridgman technique and had *p*-type conductivity [9]. The crystalline substrates were cut out from the ingot and were like the plane-parallel plates with dimensions close to 10×5×0.3...0.4 mm. These substrates were placed in an electric furnace, where they were kept for various times in air at the temperature 420 °C. The oxidation temperature was arbitrarily chosen. After thermal oxidation, the samples were investigated to ascertain oxide surface topology. The atomic force microscope Nanoscope IIIa Dimension 3000 SPM (Digital Instruments, USA) was used for this purpose.

Conducting properties of InSe intrinsic oxide were also used to prepare two types of the In₂O₃-InSe photosensitive heterostructures with a *p-n*-junction location relative to *c*: $N\parallel c$ and $N\perp c$ (*N* is the vector normal to the *p-n*-junction plane) [1]. The procedure of heterostructures preparation was as follows. Only one facet with oxide film was kept in oxidized samples. Oxides on other their facets were removed by cutting off and cleaving the corresponding end surfaces. Pure indium was used as material for ohmic contacts. The photoresponse spectra of heterostructures were investigated using the MDR-3 monochromator (Russia). A spectral resolution was not worse than 13 Å/mm. All the spectra were normalized to unity quantum efficiency.

3. Results and discussion

AFM-images of the InSe unoxidized and oxidized surfaces are shown in Fig. 1. They demonstrate that the oxide surface topology and nanoobject sizes can be varied by processing conditions when oxidizing the substrate surfaces. We considered some peculiarities of surface topology in detail. The mean arithmetic roughness value R_a was determined to be ~0.053 nm for the unoxidized surface in the plane (0001) (Fig. 1a). This value confirms a conclusion about the high quality of the crystal cleavage. After oxidation of the samples for 15 min, formed on the InSe surface are clusters of oxide

crystallites that were painted with white color in Fig. 1b. They were risen above the surface, distributed randomly and have an indefinite form. The crystallite lateral sizes reached approximately one hundred nanometers. The height of single crystallites determined by the section analysis method did not exceed 1 nm. The sizes of the unoxidized areas (dark-colored) were decreased for the samples oxidized for 1 h (Fig. 1c). The value of R_a was increased up to ~0.631 nm. The single crystallites had a look of high nano-islands. Their height attained 10 nm. Appearance of these groups of nano-islands can be related with different times of their formation on the InSe surface and peculiarities of the crystallites coalescence. The oxide crystallites transform in a more uniform ensemble of nano-islands with increasing the oxidation time up to 5 h (Fig. 1d). On the basis of statistical analysis by using the AFM-image, the surface density of nano-islands was estimated as $\sim 4 \cdot 10^9 \text{ cm}^{-2}$. The average values of the nano-islands sizes are: $h = 5.2 \pm 2.44 \text{ nm}$ and $d = 50.6 \pm 7.2 \text{ nm}$, where *h* is their height, and *d* is the diameter of their base. It should be noted that in Fig. 1d the scale of the vertical axis is 10 times less than the scale in the horizontal plane. Therefore, the real shape of these nano-islands is a low cone. After oxidation of the samples for 20 h, the oxide crystallites are transformed from a needle-shaped to dome-like shape (Fig. 1e). Their height and base attain 50 and 200 nm, respectively. Thus, the ordered nano-islands ensemble can be formed on the In₂O₃ surface by optimization of processing conditions.

The photoresponse spectra of the In₂O₃-InSe heterostructures with the nanostructured oxide are shown in Fig. 2a. They were investigated in the range of the fundamental absorption edge of light for all the oxidation regimes. The spectra for the samples with two localizations of *p-n*-junction relatively to the *c*-axis are illustrated in Fig. 2b. Dynamics of the spectra behavior in Fig. 2a consists in their long-wave shift and the appearance on them the fine structure in the form of peak as a result of changing the oxidation conditions. The greater the sizes of nano-islands and higher their ordering on the oxide surface, the more pronounced is the energy shift of the photoresponse edge and more intense is the peak in the spectrum (curve 4, Fig. 2a). A change of the surface relief in direction of decreasing its roughness results in decreasing the above peculiarities in the spectra (curve 5, Fig. 2a). The maximum value of the edge shift equals approximately 0.13 eV. To explain the results obtained involving the different topology of oxide surface, one should take into account the behavior of the photoresponse spectra of the In₂O₃-InSe heterostructures obtained for two orientations of light polarization plane: $E\perp c$ and $E\parallel c$ (Fig. 2b). One can see from Fig. 2b that the corresponding spectra are also shifted, and one of them (in the case $E\parallel c$) has a peak, too. Low-temperature investigations of the spectra have indicated that the edge peaks take place for both cases of illumination [5, 10].

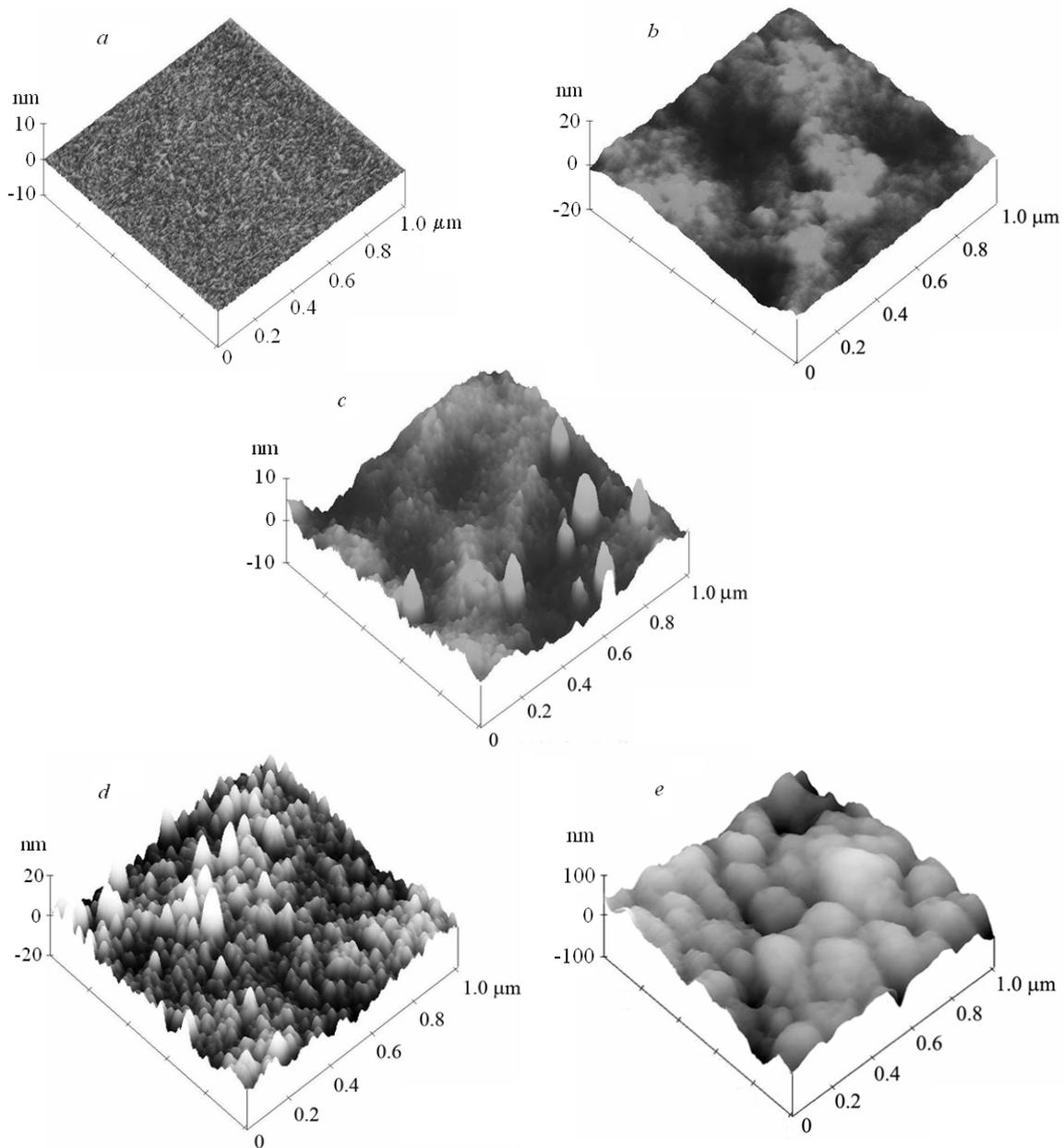


Fig. 1. AFM images of unoxidized (a) and oxidized (b-e) InSe (0001) surfaces; oxidation at 420 °C for 0.25 (b), 1 (c), 5 (d), and 20 h (e).

These peaks involve the formation of excitons. Since the exciton binding energy in InSe is also anisotropic, the peak is only observed at room temperature in the case $E\parallel c$, when $Ry > kT$ (Ry is the exciton Rydberg, k – Boltzmann constant, T – absolute temperature) [1]. The long-wave shift of the spectrum for polarization $E\parallel c$ is caused by changing a type of the interband transitions: allowed in the case $E\parallel c$ and forbidden for $E\perp c$ [11].

A comparison of these results testifies that the nanostructured surface of oxide causes diffraction of beams, i.e. it changes the angle between E and c vectors. The nano-islands ordered ensemble should be assumed to act as a diffraction network with the nanosized cells. In the case of the spectrum shown in Fig. 2a (curve 4),

the deviation of beams from their normal incidence is so great that it corresponds practically to the case of illumination of samples for polarization $E\parallel c$ (curve 1, Fig. 2b). Thus, the nanostructured surface ordered promotes to the strong diffraction of light.

The revealed properties can be used to optimize photoelectrical parameters of In_2O_3 -InSe heterostructures with the nanostructured oxide layer. Since the absorption coefficient of light in InSe is anisotropic, and it is higher in polarization $E\parallel c$ as compared with $E\perp c$, the generation region of photocarriers and the coefficient of their collection by a barrier can be essentially changed under illumination of these heterostructures.

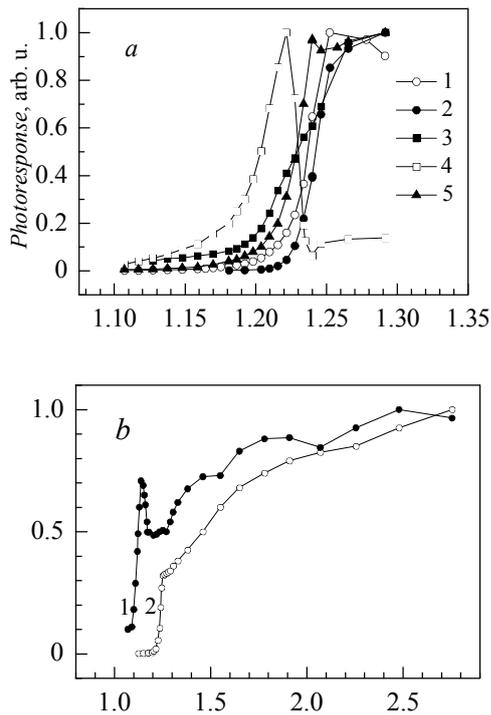


Fig. 2. Room temperature photoresponse spectra for In_2O_3 - p - InSe heterostructures at different geometry of illumination: *a*) $E \perp c$, 0 (1), 0.25 (2), 1 (3), 5 (4), and 20 h (5) oxidation time; *b*) $E \parallel c$ (1) and $E \perp c$ (2).

It should be noted that in investigated heterostructures the surface properties change of oxide and its thickness can also influence on the photoelectrical parameters of these structures. In this relation, there is of interest a future study of the influence of a surface roughness on the light reflection coefficient of oxide. The antireflection effect of oxide films on photoelectrical characteristics of structures was also not taken into account. It is related to that interference effects in the photocurrent spectra were not observed.

4. Conclusions

In_2O_3 conducting oxide films were obtained by thermal oxidation of InSe crystals at 420°C . The surface structure of the unoxidized and oxidized crystals was examined using an atomic force microscope. Topology of the surface nanoobjects was established to be changed in dependence on oxidation time. The highest order of nanoobjects like the observed ensemble of nano-islands was obtained for the samples oxidized for 5 h.

Photosensitivity and photoresponse spectra of In_2O_3 - InSe heterostructures with the oxide nanostructured surface depend on the degree of ordering the surface nanoobjects. This is indicative of diffraction properties the nanostructured surface. The higher

uniformity and ordering of nanoobjects, the stronger diffraction of beams occurs and the greater are changes in the photoresponse spectra. The changes in the spectra are analogous to those caused by orientation of samples when illuminating them with polarized light from $E \perp c$ to $E \parallel c$.

References

1. N.N. Ledentsov, V.M. Ustinov, V.A. Shchukin, P.S. Kop'ev, Zh.I. Alferov, D. Bimberg, Quantum dot heterostructures: Fabrication, properties, lasers (Review) // *Fizika Tekhnika Poluprovodn.* **32**(4), p. 385-410 (1998), in Russian.
2. R. Adelung, F. Ernst, A. Scott, M. Tabib-Azar, L. Kipp, M. Skibowski, S. Hollensteiner, E. Spiecker, W. Jäger, S. Gunst, A. Klein, W. Jägermann, V. Zaporozhchenko, F. Faupel, Self-assembled nanowire networks by deposition of copper onto layered-crystal surfaces // *Adv. Mater.* **14**(15), p. 1056-1061 (2002).
3. R.N. Bekimbetov, Yu.A. Nikolaev, V.Yu. Rud', Yu.V. Rud', E.I. Terukov, Photovoltaic effect in a - Si:H/n - InSe heterostructures // *Fizika Tekhnika Poluprovodn.* **34**(9), p. 1105-1108 (2000), in Russian.
4. V.N. Katerinchuk, M.Z. Kovalyuk, InSe heterojunctions formed by thermal oxidation of crystal substrate // *Pisma v Zhurn. Tekhn. Fiziki*, **18**(12), p. 70-72 (1992), in Russian.
5. Z.D. Kovalyuk, V.N. Katerinchuk, T.V. Betsa, Photoresponse spectral investigations for anisotropic semiconductor InSe // *Opt. Mater.* **17**(1), p. 279-281 (2001).
6. K. Uosaki, M. Koinuma, Atomic imaging of an InSe single-crystal surface with atomic force microscope // *J. Appl. Phys.* **74**(3), p. 1675-1678 (1993).
7. A.I. Dmitriev, V.V. Vishnyak, G.V. Lashkarev, V.L. Karbovskii, Z.D. Kovalyuk, A.P. Bakhtinov, Morphology analysis of the Van der Waals surface of InSe single crystals // *Fizika Tverdogo Tela*, **53**(3), p. 579-589 (2011), in Russian.
8. Z.D. Kovalyuk, V.M. Katerynchuk, A.I. Savchuk, O.S. Lytvyn, Topology of GaSe oxidized crystals // *Superlatt. Microstruct.* **44**(4-5), p. 416-419 (2008).
9. A. Segura, J.P. Guesdon, J.M. Besson, and A. Chevy, Photovoltaic effect in InSe : Application to solar energy conversion // *Rev. Phys. Appl.* **14**(1), p. 253-257 (1979).
10. J. Camassel, P. Merle, H. Mathieu, A. Chevy, Excitonic absorption edge of indium selenide // *Phys. Rev. B*, **17**(12), p. 4718-4725 (1978).
11. V.L. Bakumenko, Z.D. Kovalyuk, L.N. Kurbatov, V.F. Chishko, Optical properties of InSe single crystals in the fundamental absorption edge region. I. // *Fizika Tekhnika Poluprovodn.* **10**(6), p. 1045-1051 (1976), in Russian.