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Photosensitive sulphide heterostructures obtained by using Successive Ionic Layer Adsorption and Reaction on planar and profiled substrates

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Abstract. The photosensitive heterostructures of ZnS/SnS_x were formed by Successive Ionic Layer Adsorption and Reaction method on the nanoporous anodic alumina matrixes, on tantalum oxide nanocolumns and on planar ITO/glass substrate. Investigation of morphology of ZnS/SnS_x films layered on the substrates with different surfaces has show which the layering of functional layers has dominated horizontal deposition mechanism. It has been established that the layering of sulfides on anodic alumina proceeds with a higher rate than the layering on ITO/glass. Also ZnS/SnS_x heterostructure formed on nanoporous anodic alumina has pronounced interface between layers of sulphide compounds while in the heterostructure on ITO such interface is missing. The layering of ZnS/SnS_x heterostructure on the tantalum oxide nanocolumns occurs locally. ZnS/SnS_x/ITO/glass structure has the electrical resistance in the order of 140-80 Ohm. During illumination of the ZnS/SnS_x/ITO/glass by white light with radiation power about 11 W in structure is formed of photoelectromotive force about 230 mV.

1. Introduction

An important trend in the development of the modern optoelectronic devices is the transition from the simple materials and homojunctions to the composite materials and heterojunctions. The formation of semiconductor heterostructures with nanoscale layers allows improving the parameters of optoelectronic devices due to effects of optical quantization, over-injection also wide-gap window, as well as allows creating devices with new functional capabilities [1]. The most promising among the chalcogenide semiconductors used in optoelectronics are sulphide materials, especially the wide-gap A^{II}B^{VI} semiconductor ZnS with $E_g = 3,7$ eV and the narrow-gap A^{IV}B^{VI} semiconductor SnS with $E_g = 1,1$ eV. These sulphide compounding are characterized by low values of solubility products, which allows to use chemical deposition technologies to form optically active heterostructures based on them [2, 3].

One of the most promising and technological chemical method for the formation of active layers is the SILAR (Successive ionic layer adsorption and reaction). The SILAR method is based on layer-by-layer growth of films by periodic treatment of substrates in solutions of metal salts or polyelectrolytes. Cations and anions adsorbed on the surface of the substrate form nanolayer of low-solubility compound. Monolayer application of materials with different chemical kind by SILAR method allows precise control of the thickness and composition of the forming functional layers [4]. Earlier SILAR



method has already been successfully used in the filling of porous matrixes of anodic alumina with metal oxide compounds [5].

Profiled substrates such as porous anodic alumina and tantalum oxide nanocolumns are interesting for forming of structured systems on their base. Due to their high mechanical strength this substrates are used as matrixes for filling with different materials. The possibility to change the morphology of profiled matrices in a wide range of structural parameters allows to forming on their base of systems with defined measurements of structural elements, at that properties of those systems are determined by their measurements [6, 7].

This paper presents the results of the layering of ZnS/SnS_x heterostructures by SILAR method on the profiled anodic alumina matrix and tantalum oxide nanocolumns also on the planar indium-tin-oxide on glass substrate and investigation of morphology, electrophysical and photovoltaic properties of formed structures.

2. Experimental

2.1. Substrates for forming of ZnS/SnS_x heterostructures

Sulphide heterostructures ZnS/SnS_x were formed on the three types of substrates: 1) anodic alumina matrixes with thickness of 1 μm and pore diameters of 400 nm, 2) tantalum oxide nanocolumns with high 340 nm and diameters of columns 270 nm, 3) ITO film (In_{1.8}Sn_{0.2}O₃) with thickness 200 nm.

Nanoporous anodic alumina matrixes (AAM) were formed by multi-step anodizing of the 1.5 μm aluminium film magnetron-sputtered on the Si substrate in aqueous solution of 0.2 mol·dm⁻³ tartaric acid. On the first step anodizing were performed in galvanostatic mode at current 6 mA/cm² on thickness of Al 700 nm. After first anodizing step formed anodic alumina was selective dissolved in aqueous phosphoric-chrome solution (H₃PO₄:CrO₃:H₂O) at 80°C, which allows to structurized of aluminium surface of oxide cells imprints. On the second step anodizing were performed in potentiostatic mode at anodic potential of 213 V to form anodic alumina of thickness 1 μm. To increase the surface-to-volume ratio, AAM were subjected to pore modification in aqueous mixture of phosphoric acid and chromic oxide at 60°C during 12.5 minutes. The pore diameters were ~ 400 nm.

Tantalum oxide nanocolumns array was formed by electrochemical anodizing of two-layer Al/Ta thin-film system (1.2 μm Al and 50 nm Ta) on the Si substrate. Anodizing of the aluminum layer was performed in aqueous solution of 0.2 mol·dm⁻³ tartaric acid at voltage of 216 V. Tantalum oxide nanocolumns were formed by high-voltage reanodizing of the niobium layer via formed AAM in the mixed solution of 0.5 mol·dm⁻³ boracic acid and 0.05 mol·dm⁻³ sodium tetraborate in potentiodynamic mode at increase of potential until 450 V. Further AAM was selective dissolved in 50% phosphoric acid at 50°C.

2.2. SILAR method for layering of ZnS/SnS_x on substrates with different surfaces

ZnS/SnS_x heterostructures were deposited on the anodic alumina matrixes, array of tantalum oxide nanocolumns and ITO/glass substrate by SILAR method. The main stages of the formation of film structures are shown in Figure 1. On the first step substrates were cleaning in deionized water (T = 90–100°C) or in polar organic solvents (Figure 1, a). Next on the substrates were layered Sn-cations from solution 0.1 mol·dm⁻³ SnCl₂ (Figure 1, b) and S-anions from solution 0.1 mol·dm⁻³ Na₂S (Figure 1, d). After cationic and anionic layering steps the substrates were washed in deionized water at T = 20°C (Figure 1, c, e). So was formed one microlayer of SnS_x. The layering of cations and anions was repeated 20 times for each layer, as a result were formed 20 microlayers of SnS_x. After that substrates were dried at T = 50°C for 30 min and annealed at T = 350°C for 30 min (Figure 1, f). On SnS_x layers were formed 20 microlayers of ZnS by sequential layering of Zn-cations from solution 0.1 mol·dm⁻³ ZnSO₄·7H₂O (Figure 1, g) and S-anions from solution 0.1 mol·dm⁻³ Na₂S (Figure 1, i) with washing substrates in deionized water (T = 20°C) after each layering step (Figure 1, h, j). After layering of cations and anions substrates were dried at T = 50°C for 30 min and annealed at T = 350°C for 30 min (Figure 1, k).

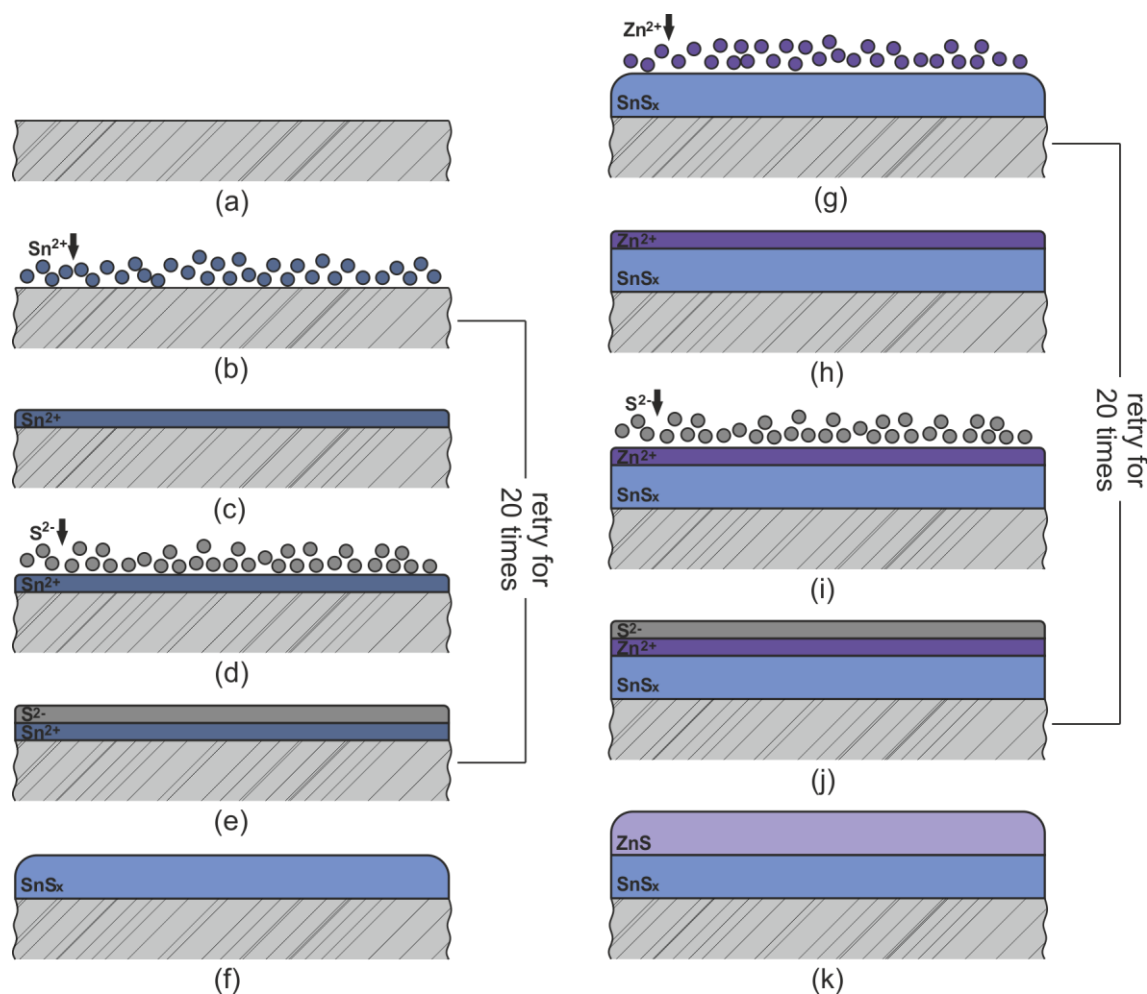


Figure 1. Schematic steps for forming of ZnS/SnS_x heterostructures: **(a)** cleaning of the substrate surface; **(b)** layering of Sn²⁺ ions from solution 0.1 mol·dm⁻³SnCl₂; **(c)** washing in deionized water; **(d)** layering of S²⁻ ions from solution 0.1 mol·dm⁻³Na₂S; **(e)** washing in deionized water; **(f)** drying at T = 50°C, annealing at T = 350°C; **(g)** layering of Zn²⁺ ions from solution 0.1 mol·dm⁻³ZnSO₄·7H₂O; **(h)** washing in deionized water; **(i)** layering of S²⁻ ions from solution 0.1 mol·dm⁻³Na₂S; **(j)** washing in deionized water; **(k)** drying at T = 50°C, annealing at T = 350°C.

3. Results and discussion

3.1. Investigation of morphology of ZnS/SnS_x films layered on the substrates with different surfaces

In the Figure 2 presented the cross-sections of the nanoporous AAM (Figure 2, a), tantalum oxide nanocolumns (Figure 2, b) and ITO/glass substrate (Figure 2, c) with layered thin film system of ZnS/SnS_x. Investigation of the ionic layering of ZnS/SnS_x films on the substrates with different surface morphology has shown that the layering of functional layers has dominated horizontal deposition mechanism, which leads to the formation of planar layer on the profiled matrix (Figure 2, a, b). It should be noted that formation of ZnS/SnS_x on the planar ITO substrate (Figure 2, c) occurs only after the washing in polar organic solvents and ultrasonic treatment of the substrate surface.

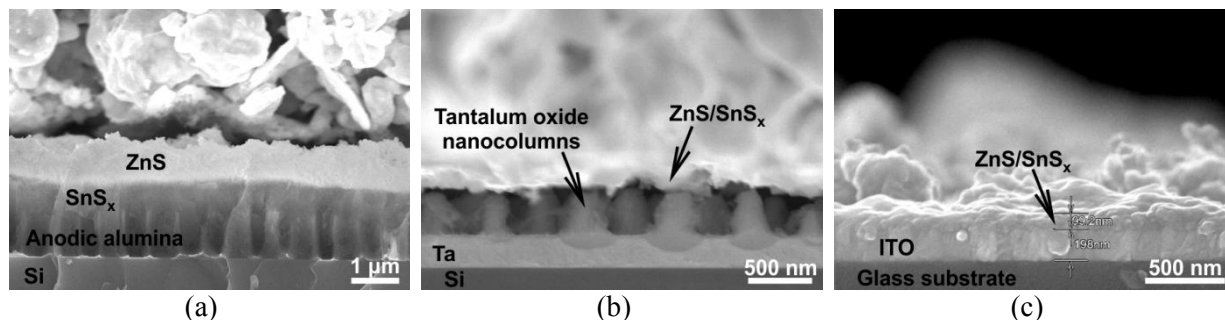


Figure 2. SEM microphotographs of the cross-section of the ZnS/SnS_x heterostructures on (a) anodic alumina matrix, (b) tantalum oxide nanocolumns, (c) ITO/glass substrate.

ZnS/SnS_x heterostructure formed on nanoporous AAM has pronounced interface between layers of sulphide compounds (Figure 2, a). That allows estimated thicknesses of sulphide layers, which amounted to about 600 nm for SnS_x and about 870 nm for ZnS. Given that the nominal quantity of the microlayers for the each sulphide compounds was the same and amounted to 20, it can be noted that the layering of SnS_x on the profiled surface of the chemically foreign Al₂O₃ proceeds with significantly less speed than the of layering of ZnS on the surface of chemically similar SnS_x. The calculated thicknesses of microlayers for SnS_x was about 30 nm and for ZnS – about 43,5 nm. We note that in our previous experiments in separate layering of SnS_x and ZnS layers on the surface of porous AAM, we obtained an analogous result about more less speed of deposition of SnS_x [8].

The total thickness of the sulphide heterostructures formed on the surface of the ITO film with thickness of 200 nm was about 100 nm (Figure 2, c). So there has been significant decrease of layering speed on the planar ITO substrate in comparison with the profiled AAM substrate, which leads to decrease of the average thicknesses of microlayers of SnS_x and ZnS to 2.5 nm. Such result can be accounted for removal of excess precursor solutions from surface of planar substrate, which allows realize the ionic layering in mode of monolayer film growth with precision control of its thickness.

The layering of heterostructures on the tantalum oxide nanocolumns array occurred locally. On the local areas of the substrate surface were formed ZnS/SnS_x films (Figure 2, b), the formation of continued film did not occur. Probably, as in the case of planar ITO substrate, the hydrate treatment of the nanocolumns array do not allows to get surface, which is chemically usable to ion layering.

3.2. The electrophysical investigations of formed heterostructures

Investigations of the electrophysical and photosensitive properties of sulfide heterostructures were pursued on the planar ITO/glass substrates, which has the necessary transparency.

The electron transport properties of heterostructures were researched by measuring of the temperature dependences of the surface electrical resistance of sulphide films (Figure 3).

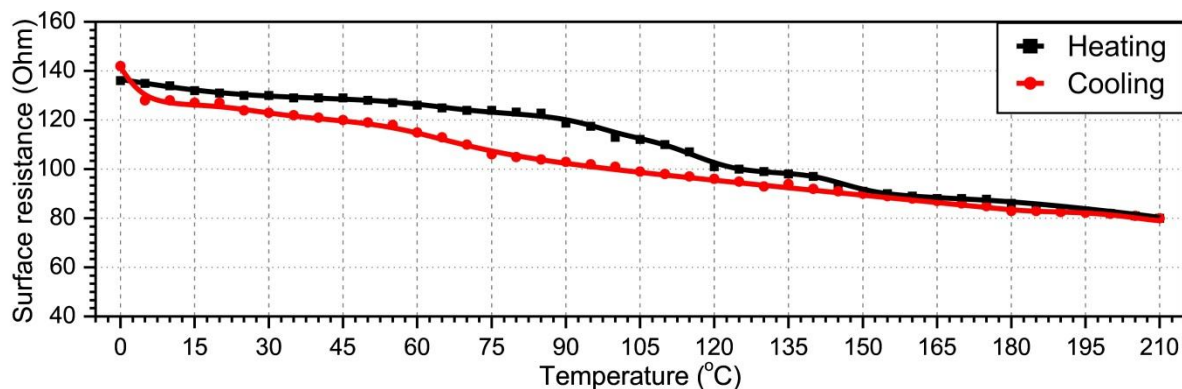


Figure 3. Temperature dependences of the surface resistance of ZnS/SnS_x/ITO/glass structure

The measurements were pursued in special installation, which included measuring cell, two voltmeters and current source. Heterostructures were placed in a measuring cell with clamping electrodes on the resistive heating element based on a nichrome wire. The measurements were carried out in the temperature range from 0 to 210°C. Investigations of the electrophysical properties showed that the planar structure of ZnS/SnS_x/ITO/glass substrate is characterized by a low electrical resistance in the order of 140-80 Ohm. Temperature dependence of the surface electrical resistance of formed structures has semiconductor character with weak hysteresis phenomena.

Photosensitive ZnS/SnS_x heterostructure amounts to wide-gap window in the form of ZnS and absorptive narrow-gap layer SnS_x. The effect of the radiation power on the value of the generated photoelectromotive force on illumination of the heterostructure by white light was investigated. An incandescent lamp with an adjustable radiation power from 0 to 12 W was used as light source. The voltage difference, which appeared in the heterostructure during illumination by incandescent lamp, was measured. In the Figure 4, a shown schematic view of investigational heterostructure. Value of the photoelectromotive force was measured under illumination of different areas of heterostructure: ZnS/SnS_x/ITO structure with large (Figure 4, a, contacts a-c) and small (Figure 4, a, contacts a-b) working surface area, surfaces film ZnS (Figure 4, a, contacts b-c), ITO (Figure 4, a, contact a). Dependence of the photoelectromotive force of heterostructure on the radiation power shows in Figure 4, b

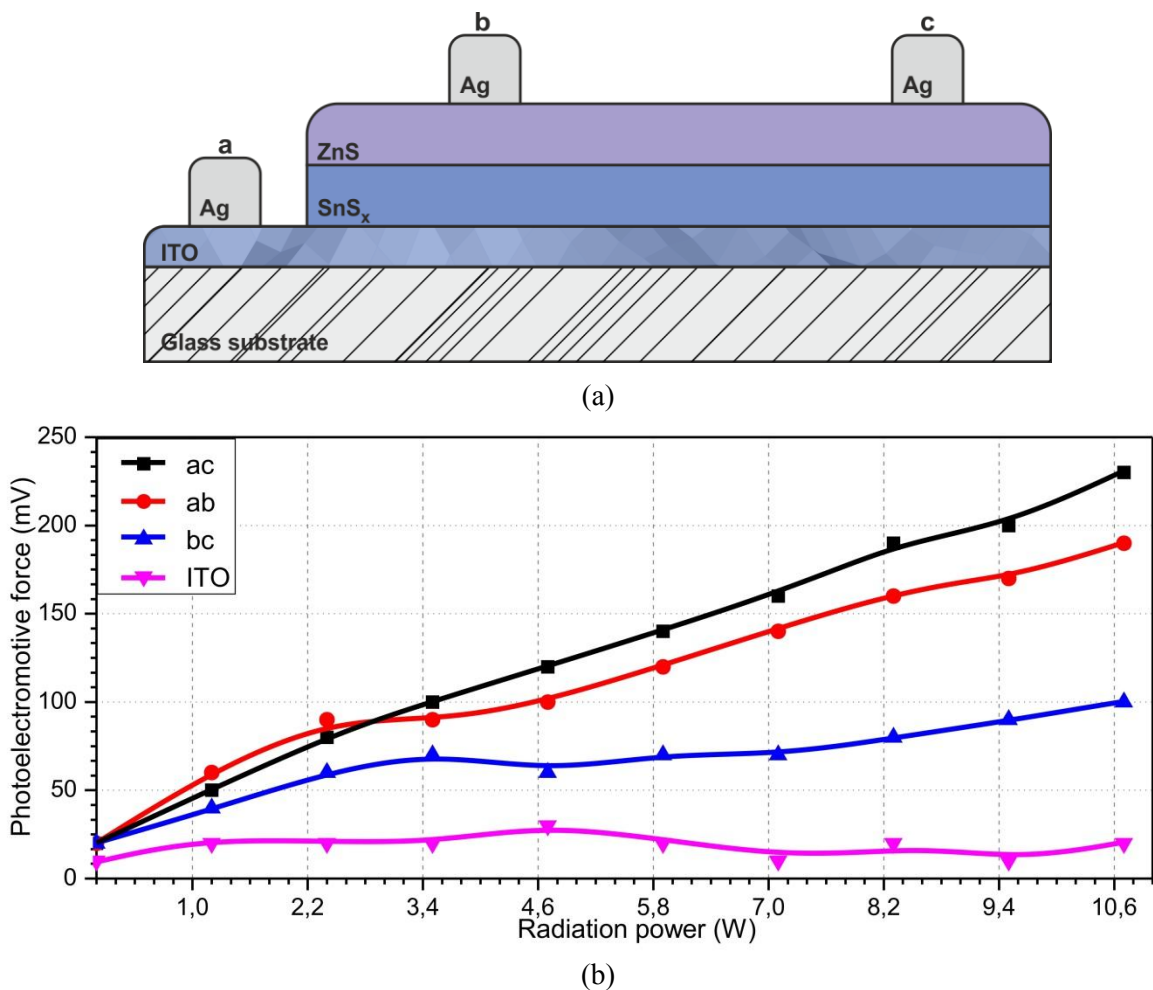


Figure 4.(a) Schematic view of ZnS/SnS_x/ITO/glass heterostructure with different working areas; (b) Dependence of the photoelectromotive force, generated in the ZnS/SnS_x heterostructure, on the radiation power during illumination of different working areas.

As is seen from received dependences photoelectromotive force was increasing under increase of the power of the white light source. Character of photoelectromotive force increasing was close to monotonic. The most significant photoelectromotive force close to 230 mV was generated during illumination of the large working surface area of the structure (Figure 4, b, curve a-c). Value of photoelectromotive force, which was generated during illumination of the small working surface area of the structure, was about 190 mV (Figure 4, b, curve a-b). Voltage differences which were generated during illumination surfaces film ZnS (Figure 4, b, curve b-c) and ITO (Figure 4, b, curve ITO) did not exceed 100 mV (about 90 mV for ZnS and about 20 mV for ITO). This can be explained by the appearance of a volumetric photoelectromotive force which has significantly lower value than barrier-layer photoelectromotive force appearing near the potential barrier of a functional contact.

4. Conclusion

So, in this work were presented the results of the obtaining of sulphide ZnS/SnS_x heterostructures by using Successive Ionic Layer Adsorption and Reaction method on the planar ITO/glass and profiled anodic alumina also tantalum oxide nanocolumns substrates. Layering of the ZnS/SnS_x on the ITO/glass substrate was realized in monolayer films growth mode, thickness of the formed heterostructure was about 100 nm. ZnS/SnS_x heterostructure formed on nanoporous anodic alumina was characterized by pronounced interface between layers of sulphide compounds. Thicknesses of sulphide layers were about 600 nm for SnS_x and about 870 nm for ZnS. The continued ZnS/SnS_x films did not occur during the layering on the tantalum oxide nanocolumns. Forming of the heterostructures was occurred on the local areas of the substrate surface.

Investigations of the electrophysical properties of planar transparent ZnS/SnS_x/ITO/glass structures shown the electrical resistance in the order of 140-80 Ohm. Photovoltaic measurements during illumination of the ZnS/SnS_x/ITO/glass structure by white light with radiation power about 11 W shown the forming of photoelectromotive force about 230 mV in the functional contacts. This value is 35% higher than the result for similar structure obtained by electrochemical deposition [2]. The obtained results show the prospects of using the SILAR method for obtaining photoactive sulfide heterostructures on planar and profiled substrates. ZnS/SnS_x heterostructures can be used in low-cost thin-film solar cell.

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