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INVESTIGATION OF CHEMICAL AND PHASE COMPOSITION OF CdS-Cu₂S SENSORIC LAYERS

A set of studies aimed at clarifying the deviation from the stoichiometry of Cu_xS compound during the formation and followed over time to establish the characteristics of changes in the chemical composition of the heterojunction components were carried out. The question of relationship between optoelectrical properties of heterostructures and distribution of stoichiometry in the layer of copper sulfide is open, informative and very important for the practical implementation of the developed sensor. Electrochemical analysis and study by X-ray diffraction for large samples set were conducted

Key words: nonideal heterojunction, image sensor, phase composition, XRD

Introduction

Development of technologies for the synthesis of thin film semiconductor materials led to a wide range of application of opto-mechanical and electrical properties of the instrument in the field of electronics, such as further study actively used in the technological aspect Semiconductor is important. In particular among these compounds are attracted interest for modeling the properties and development of various applications applied heterostructures on the cadmium sulfide (CdS) and copper sulfide (Cu₂S), which can serve as the core material photodetectors for use in optical communication devices, particularly in the infrared region spectrum.

In addition, some marked prospects of these nonideal heterostructures in devices fixation ray images [1]. Another area of application material CdS-Cu₂S moving towards the development of new gas-chemical sensors [2]. It describes the main advantages of these prototypes sensors: selective gas detection sensitivity and modes of operation at low temperatures.

Thus one of the characteristics of photosensitive heterostructures on the CdS-Cu₂S is the in-

stability of photovoltaic parameters during operation. Eventually decrease circuit voltage and short circuit current, ie the sensor signal with the same levels of photoexcitation decreases in service. Consequently, there is a degradation over time as heterojunction photovoltaic, which can be associated with changes in both the structure element and component properties of films of transition. It is this negative phenomenon becomes an obstacle and a problem with the possible use of these heterostructures for practical applications in sensorics. However, none of the technologies used, does not get photocells released (without the involvement of special protection) from degradation.

It was discovered experimentally [3-5] that chemical methods of sulfide copper-based substitution reaction on the surface of cadmium sulfide lead to the formation of nonstoichiometric compounds Cu_xS. Depending on the reaction conditions the value of x can vary from 1 to 2. It is known that at room temperature phase are more stable sulfide copper halkotsyt - Cu₂S; dyurlit - Cu_{1.96}S; dihenyt - Cu_{1.8}S; anilit - Cu_{1.75}S; kovelit - CuS. Typically, between different phases form a solid solution. Each phase can be deviations from stoichiometry, which causes changes in physical

properties such as crystal lattice parameters, optical and electrical steel. [4] These property changes can be used for determination of bulk samples, and for variations in the properties of sensors based heterostructures CdS-CuS [6]. In the case of thin films and small amount of test material the use of direct techniques of chemical analysis is very complicated.

X-ray diffractometry analysis

Using electrochemical analysis to clarify the mechanisms change with time stoichiometry layer CuS actually proved inconclusive due to the presence of layers simultaneously studied a number of phases with different concentrations of Cu. So for samples that have undergone degradation caused by changing the chemical composition of copper sulfide layer in the electrochemical reduction reaction involved once all steps to separate phases and potential recovery due to varying phase, almost impossible, because they are imposed on the initial section of the recovery.

So for more information on changing the stoichiometry and phase composition distribution layer Cu_xS studied sensory structures under its degradation over time used the method of phase diffraction analysis [8]. It was involved X-ray diffractometer D8 Advance (Bruker AXS) with emission lines Cu K (wavelength 1.54183 Å, the working potential of the cathode Ua 40 kV, Ia cathodic current 40 mA).

We used scanning modes geometrically symmetric and scanning with a sliding beam falling (GIXRD). In the latter case the angle recorded at the value 0.5, diffraction pattern measured in the range of 20 to 80 mode step scanning step size 0.04, while fixing signal for 5 seconds. Processing and analysis of diffraction spectra was carried out using software Bruker-AXS EVA (11.0.0.3), for modeling spectrograms and further define the parameters studied layers used program Bruker-AXS TOPAS 3.0. Features component composition were studied using pattern database Joint Committee on Powder Diffraction Standards (JCPDS) [8].

For separation of the diffraction peaks due to the different layers of compounds present in the

sample, ie contact layer SnO_2 , base area and upper CdS films Cu_xS , and in some cases - the upper contact layer Cu or Au, diffraction scans were conducted separately for samples with only a layer of cadmium sulfide, for samples with pre-deposited on the substrate layer and SnO_2 sample formed with a layer of copper sulfide.

Results and discussion

Radiometric research base layer samples of CdS on a glass substrate with pre-deposited layer of tin oxide allowed to identify distinct diffraction peaks corresponding to these compounds. For spectrum in CdS was the most appropriate JCPDS-41-1049 file corresponding hexagonal lattice of CdS and the constant = 4.14092 Å, $p = 6.7198$ Å (Fig. 1). According to the comparative pattern JCPDS 41-1049, clear peaks were observed reflections for the crystallographic planes of the following indexes: (100) (002) (101) (102) (110) (103) (112) (004) (203) (114) (105).

During the analysis for each of the superimposed diffraction patterns obtained from the database directory JCPDS, corresponding to potentially available connections and fixed convergence in positions of diffraction peaks experimental data directory [8]. Used comparatives files related to sulfur, copper, oxygen, chlorine (could partly be in bed with incomplete substitution reaction), oxygen (possible oxidation of copper sulfide oxygen atmosphere): JCPDS 33-490 (Cu_2S), JCPDS 29-0578 ($Cu_{1.96}S$), JCPDS 34-0660 ($Cu_{31}S_{16}$), JCPDS 30-0502 ($Cu_{1.92}S$), JCPDS 41-0959 ($Cu_{1.81}S$), JCPDS 23-0958 (Cu_7S_4), JCPDS 06-0464 (CuS), JCPDS 44 -4750 (CuCl), JCPDS 36-5511 (Cu_2O). An example of a typical type of distribution relative intensities of the diffraction peaks of the diffraction angle obtained during scanning newly made and old samples CdS- Cu_xS , presented at ryc. 3, which also marked the position of peaks for compounds of hexagonal CdS and various phases of Cu_xS . Thus was the comparative analysis of the diffraction pattern in terms of identifying compounds present in the samples of all ages. The new samples were detected the possible presence of these copper sulfide phases: Cu_2S , $Cu_{1.96}S$, $Cu_{1.92}S$, Cu_7S_4 .

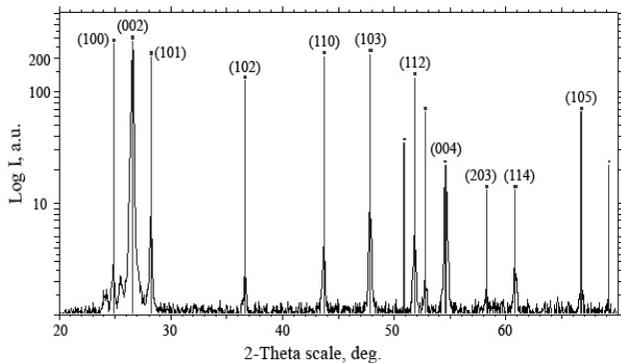


Fig. 1. Diffraction peaks for CdS layer on a glass substrate obtained by sputtering elektrohdrodynamichnoho. Marked provisions peaks for hexagonal CdS and the corresponding crystallographic indexes according to Comparative File JCPDS 41-1049.

For older specimens observed a wide range of diffraction peaks that meet the following phases: Cu_2S , $\text{Cu}_{1.96}\text{S}$, CuS . Peaks corresponding to the compounds CuCl and Cu_2O , were not found.

After counting all the relevant peak was obtained comparative table, which indicated the number of peaks of each phase Cu_xS for a new sample and the sample aged 3 years. Evident differences in the composition of new and old sensory elements. This indicates the presence of the process of gradual change in the phase composition of copper sulfide layer, and thus likely outflow of copper from the compound Cu_xS over time. This process may be responsible for changing the stoichiometric Cu_2S layer heterojunction $\text{CdS-Cu}_2\text{S}$.

It is known [9] that copper atoms in the crystal lattice have the ability to form CdS acceptor centers that may compensate donor impurities initially present in the base layer. Also listed copper diffusion process along the borders of microcrystalline grains can cause the base effect bypass area. Note that in the investigated heterostructures reliably observed change stoichiometric copper sulfide layer svitlopohlynayuchoho emergence of a number of phases Cu_hS . Available for the process paths are: oxidation Cu_2S to Cu_2O by oxygen, electric Cu_2S decomposition with the release of free copper atoms and diffusion of copper into the

crystal lattice Cu_2S CdS lattice as free atoms and formation of complexes.

Conclusion

Used diffractometry research methodology significantly helped to establish the existence of a number of phases in the non-stoichiometric copper sulfide layer and to make a comparative analysis of the phase distribution for samples of different ages and varying degrees of degradation. It was demonstrated that used in this paper methods of analysis phase composition of copper sulfide layers give unambiguous characterization of the degree of degradation with time sensor samples due to diffusion of copper atoms from the layer to the base layer $\text{Cu}_x\text{S-CdS}$.

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MODELLING OF RAPID STAGE DECAY OF SIGNAL OF OPTICAL SENSOR BASED ON HETEROSTRUCTURE CdS-Cu₂S

Summary. A set of studies aimed at clarifying the deviation from the stoichiometry of Cu_xS compound during the formation and followed over time to establish the characteristics of changes in the chemical composition of the heterojunction components were carried out. The question of relationship between optoelectrical properties of heterostructures and distribution of stoichiometry in the layer of copper sulfide is open, informative and very important for the practical implementation of the developed sensor. Electrochemical analysis and study by X-ray diffraction for large samples set were conducted.

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МОДЕЛЮВАННЯ ШВИДКОЇ ФАЗИ СПАДУ СИГНАЛУ ОПТИЧНОГО СЕНСОРУ НА ОСНОВІ ГЕТЕРОСТРУКТУРИ CdS-Cu₂S

Анотація. Робота присвячена комплексу досліджень, направлених на з'ясування відхилень від стехіометрії сполуки Cu_xS при її формуванні та з подальшим плином часу для встановлення особливостей зміни хімічного складу компонентів гетеропереходу. Враховуючи, що питання про зв'язок ступеню та розподілу стехіометрії в шарі сульфіді міді з оптоелектричними властивостями гетероструктури є відкритим, інформативним та надзвичайно важливим для

практичного впровадження розробленого сенсору, для великої вибірки зразків були проведені електрохімічний аналіз та дослідження методом рентгенівської дифрактометрії.

Ключові слова: неідеальний гетероперехід, сенсор зображень, фазовий склад, рентгеноструктурний аналіз

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МОДЕЛИРОВАНИЕ БЫСТРОЙ ФАЗЫ СПАДА СИГНАЛА ОПТИЧЕСКОГО СЕНСОРА НА ОСНОВЕ ГЕТЕРОСТРУКТУРЫ CdS-Cu₂S

Аннотация

Работа посвящена комплексу исследований, направленных на выяснение отклонений от стехиометрии соединения Cu_xS при формировании и с последующим течением времени для установления особенностей изменения химического состава компонентов гетероперехода. Учитывая, что вопрос о связи степени и распределения стехиометрии в слое сульфида меди с оптоэлектрическими свойствами гетероструктуры является открытым, информативным и чрезвычайно важным для практического внедрения разработанного сенсора, для большой выборки образцов были проведены электрохимический анализ и исследования методом рентгеновской дифрактометрии.

Ключевые слова: неидеальный гетеропереход, сенсор изображений, фазовый состав, рентгеноструктурный анализ