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MICROSTRUCTURAL FEATURES AND COMPONENTIAL ANALYSIS OF THIN FILM CdS-Cu_2S PHOTOSENSING STRUCTURES AS ELEMENT OF IMAGE SENSOR

The mechanisms of signal relaxation, associated with the removal processes of nonequilibrium charge from the space charge region of the image sensor on the basis of non-ideal heterojunction were investigated. The mechanism of the observed two-stage process was determined. Microscopic techniques (AFM, SEM) were used to estimate heterojunction properties (grain size, roughness) and their relations with heterojunction processing parameters. Novel results concerning CdS-Cu2S heterojunction surface morphology and impurities depth distribution were obtained. In particular, the question of observed variation of surface photosensitivity and components interdiffusion on heteroborder were clarified. Also the comparison of samples formed by two different methodics (electrodynamical spraying and vacuum evaporation techniques) was made. X-Ray diffraction (XRD) was performed in order to detect Cu–S compounds at CdS – Cu2S heterojunctions, fabricated by the vacuum deposition of CdS on a glass substrate and Cu2S layer, formed in substitution mode. The distribution of several stoichiometric phases of copper (I) sulfide was obtained as main result.

Heterojunction (HJ) structures can serve as basic material of photodetectors for use in optical communication applications [1]. HJ structure between p-type Cu_2S and n-type CdS is a rather complicated system because of the interface between two materials with different band gaps and crystal structure. Nonideality of considered CdS-Cu_2S structure causes the effect of photon induced modulation of HJ potential barrier, that can be used in opto-sensorics and X-ray imaging applications [2, 3]. High spatial resolution, signal storage and large working surface are reported as main advantages of obtained sensor.

The mechanisms of signal relaxation, associated with the removal processes of nonequilibrium charge from the space charge region of the image sensor on the basis of non-ideal heterojunction were investigated. The mechanism of the observed two-stage process was determined: phase of slow relaxation - implementation of the thermal emission of localized charge, that depends on temperature; phase of rapid relaxation - the result of tunneling mechanism of ejection.

CdS- Cu_2S is considered as an interesting compound for photovoltaic applications. Thin film CdS- Cu_2S sells are reported to have conversion efficiency of more than 9%, low cost and easy fabrication [4].

However, the heterojunction structure between p-type Cu_2S and n-type CdS is a rather complicated system because of the interface between two materials with different electron affinities, band gaps and crystal structures. The lattice mismatch and interdiffusion of components cause defect states at or near the interface that strongly affect the junction properties. In particular, there is Cu diffusion into the CdS adjacent to the interface, which leads to stoichiometry changing of CuxS layer and may cause shunting effect in CdS layer. But this process can be used also in positive way.

In [5] the possibility of controlling the phase structure, composition, and stoichiometry of Cu_xS

films is discussed. This enables changing certain optoelectronic properties of studied material for the fabrication of devices such as nanoscale switches, sensors, and solar cells.

The research of current transfer processes in nonideal geteropare CdS-Cu_2S allowed developing image sensor in the X-rays and optical range with high sensitivity and possibility of signal accumulation [3, 6].

The data-storage time and sensitivity of the sensor are determined by relaxation time of non-equilibrium positive charge. Possible ways of captured by traps holes removing from the barrier of non-ideal heterojunction were considered: the thermal holes emission to the CdS valence band; direct holes tunneling from trapping centers to the Cu_2S valence band; two-stage free-electron tunneling from CdS quasi-neutral region to the space charge region and subsequent recombination with nonequilibrium hole; tunnel-hopping recombination.

Relaxation curves of short-circuit current at different points of the sensor were obtained experimentally. The relaxation curve has two well-marked area: rapid initial photocurrent drop and then its relatively slow decay. At different points signal showed decrease with the same characteristic relaxation time, but very different in magnitude. This suggests, that sensor heterogeneity on the photosensitivity is caused by a substantial change of trapping centers concentration along the surface, that determine the thermal emission probability.

To clarify mechanisms implemented by charge release, sensor signal relaxation characteristics at different temperatures were studied. The time constants of later relaxation stage decrease with temperature increasing. This shows the implementation of thermal mechanism, which determines relaxation kinetics at this region. Relaxation time constants derived from experimental data and theoretical calculations are in good agreement and demonstrate the same temperature dependence. Thus, the current relaxation in considered part of current dependence is determined exceptionally by thermal charge emission from the deep hole traps.

The magnitude and the slope of initial part of the photocurrent decay don't depend on temperature. This demonstrates the implementation of photocurrent relaxation mechanism in this region, which isn't due to the thermal release and has apparently, tunneling character. Assessing the contribution of tunneling mechanisms in trapped charge relaxation was carried out by calculating the barriers tunneling transparency for the corresponding transitions. Calculations were made taking into account the changes of potential barrier shape under illumination [7]. The lack of temperature dependence of relaxation curve is due to the fact, that the values of barriers tunneling transparency don't depend on temperature. Account of tunneling processes leads to characteristics harmonization of the short-circuit current relaxation curves obtained experimentally and theoretically.

Experimentally observed phenomenon of investigated sensor signals relaxation considered and analyzed theoretically within the model of relaxation processes in the heterojunction CdS-Cu_2S.

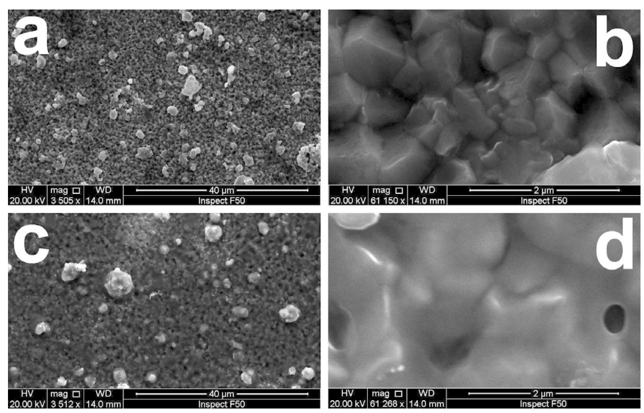

Fig. 1. **SEM scanning results for surface of sample, obtained by electro-hydrodynamic spraying methodics: CdS surface (a, b), Cu_2S surface (c, d) under 3500^x (a, c) and $60\ 000^x$ (b, d) zooming**

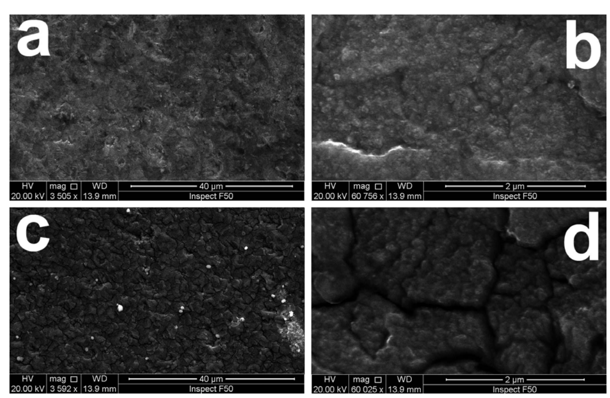

Fig. **2. SEM scanning results for surface of sample, obtained by vacuum evaporation methodics: CdS surface (a, b), Cu_2S surface (c, d) under 3500^x (a, c) and $60\ 000^x$ (b, d) zooming**

Obtained results enable to understand better the features of HJ layers forming procedure, the junction components surface interaction and influence of external environment on sensor samples surface characteristics.

Also, various microscopic techniques (AFM, SEM) were used to estimate HJ properties (grain size, roughness, luminescence depth distribution) and their relations with HJ processing parameters

The revealed differences in doping and traps densities, which lead to significant variations of electrical characteristics of junctions, can be ascribed to layer deposition regimes, to layer thicknesses and chemical combination of present compounds.

Main parameters – substrate temperature and deposition time were varied during films forming process. Thickness of base layer defines its resistivity and size of formed microctystalls.

X-Ray diffraction (XRD) was performed in order to detect Cu–S compounds at CdS – Cu_2S heterojunctions, fabricated by the vacuum deposition of CdS on a glass substrate and Cu_2S layer, formed in substitution mode.

Also phase composition of the deposits was examined by an X-ray diffractometer D8 Advance (Bruker AXS) with Cu K_α radiation (λ=1.54183 Å, U_a= 40 kV, I_a= 40 mA) separated by a curved multilayer monochromator mounted on the primary beam.

Fig. 3. XRD pattern of CdS-Cu_xS HJ sample (t_{dep} = 8 min, T_{sb} = 220º C)

Symmetrical Θ/2Θ geometry and grazing incidence (GIXRD) techniques were used and in the latter case the incidence angle (Θ angle) was 0.5°. The XRD patterns were measured in 2Θ range from 20 to 70° in a step scan mode: a step size (Δ2Θ) 0.04°, counting duration 5 s.

The diffraction angles some of main peaks corresponded to those of hexagonal CdS, and their relative peak intensities were also similar to those of the CdS (Fig. 3).

In XRD investigations of considered samples stoichiometry changing in copper sulphide layer was observed. Figure 3 show the diffraction angles and relative intensities of the XRD peaks of the CdS-Cu_xS films measured experimentally in this study. Each arrow shows the peak that correspond to possible written compounds (diffraction angles taken from JCPDS cards).

$Cu_{1.96}S$, $Cu_{1.92}S$, $Cu_{1.81}S$ and other modifications together with Cu_2S were detected (Table. 1). So in this case copper atoms diffuse from the Cu_xS layer to base CdS layer during the fabrication process and later with time. These impurities can create acceptor centres, which compensate or even overcompensate for the initially existent donors in CdS [8].

Table. 1.

Number of XRD peaks for different compounds in CdS-Cu_xS HJ

Cu_xS compound	**Number of peaks**
monoclinic Cu_2S (chalcocite)	5
tetragonal $Cu_{1.96}S$	2
monoclinic $Cu_{31}S_{16}$ (djurleite)	3
hexagonal $Cu_{1.92}S$	3
tetragonal $Cu_{1.81}S$	3
hexagonal Cu_9S_5 (digenite)	0
monoclinic Cu_7S_4 (roxbyite)	10
orthorombic Cu_7S_4 (anilite)	1
hexagonal CuS (covellite).	0

Also Cu diffusion between grain borders of CdS microcrystalls can cause shunting effect. Changing of Cu diffusion conditions (and as a result variations in electrical characterisitics) is directly connected with deposition time t_{dep} and substrate temperature T_{sb}. This initial thermal treatment defines first level of diffusion intensity and depth. It's seen, that more Cu_xS phases in samples are observed (Fig. 3). For these samples t_{dep} and T_{sb} were maximised.

Diffusion process may continue and later, at room temperature. That is confirmed by observed degradation of samples photoelectric properties with the time.

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Key words: heterojunction, image sensor, surface morphology, XRD analysis

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МИКРОСТРУКТУРНЫЕ ОСОБЕННОСТИ И КОМПОНЕНТНЫЙ АНАЛИЗ ТОНКОПЛЁНОЧНЫХ ФОТОЧУВСТВИТЕЛЬНЫХ ЭЛЕМЕНТОВ CdS-Cu_2S

Резюме

В работе были исследованы механизмы релаксации сигнала, связанные с процессами удаления неравновесного заряда из области пространственного заряда сенсора изображения на основе неидеального гетероперехода и их связь со структурными особенностями и компонентным составом образцов. Были использована комбинация микроскопических методик (АСМ, РЭМ) для оценки морфологических свойств поверхности (размер зерна, шероховатость) и их отношений с технологическими параметрами при получении гетероструктур. Были получены новые результаты, касающиеся морфологии поверхности и глубины распределения примесей. В частности, были уточнены вопросы о наблюдаемом изменении фоточувствительности поверхности и взаимной диффузии компонентов на гетерогранице. Кроме того, проведено сравнение образцов, полученных двумя различными методиками (электродинамическое распыление раствора методы вакуумного испарения). Также применялся рентгеноструктурный анализ с целью выявления различных фаз Cu-S в гетеропереходах, изготовленных вакуумным напылением на стеклянной подложке. В качестве основного результата получено распределение стехиометрических фаз сульфида меди (I) в исследуемых сенсорных структурах.

Ключевые слова: гетеропереход, сенсор изображения, релаксация сигнала, морфология поверхности, рентгеноструктурный анализ

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МІКРОСТРУКТУРНІ ОСОБЛИВОСТІ ТА КОМПОНЕНТНИЙ АНАЛІЗ ТОНКОПЛІВКОВИХ ФОТОЧУТЛИВИХ ЕЛЕМЕНТІВ CdS-Cu_2S

Резюме

У роботі були досліджені механізми релаксації сигналу, пов'язані з процесами видалення нерівноважного заряду з області просторового заряду сенсора зображення на основі неідеального гетероперехода та їх зв'язок із структурними особливостями і компонентним складом зразків . Була використана комбінація мікроскопічних методик (АСМ , РЕМ) для оцінки морфологічних особливостей поверхні (розмір зерна , шорсткість) та їх зв'язку з технологічними параметрами при формуванні гетероструктур. Були отримані нові результати, що стосуються морфології поверхні і глибини розподілу домішок . Зокрема , були уточнені питання про спостережувану зміну фоточутливості поверхні і взаємну дифузію компонентів на гетерограниці. Крім того, проведено порівняння зразків, отриманих двома різними методиками (електродинамічне розпилювання розчину та метод вакуумного випаровування). Також застосовувався рентгеноструктурний аналіз з метою виявлення різних фаз сполуки Cu-S у гетеропереходах, виготовлених вакуумним напиленням на скляній підкладці. В якості основного результату отримано розподіл стехіометричних фаз сульфіду міді (I) в досліджуваних сенсорних структурах.

Ключові слова: гетероперехід, сенсор зображення, релаксація сигналу, морфологія поверхні, рентгеноструктурний аналіз