Influence of components ratio in heterogeneous CdS-PbS material on photoelectric characteristics and their stability over time

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The effect of the ratio of CdS and PbS components on the surface morphology, optical and photoelectric characteristics of films obtained by hydrochemical deposition has been studied. It is shown that, depending on the predominance of CdS or PbS in the film, the surface morphology changes significantly, which correlates with changes in the optical and photoelectric characteristics. An increase in the stability of photoelectric characteristics is demonstrated only by samples with a predominance of CdS. When PbS predominates, photoquenching and slow relaxation of the dark current after illumination are observed.

Keywords: heterophase structures, limited solubility, optical and photoelectric characteristics, IR quenching.

Semiconductor materials and structures based on metal sulfides occupy an important place in modern electronics, due to the diversity of their electrical and optical properties. One such compound is CdS, which is used in photovoltaic transducers and other micro- and optoelectronics devices. However, photodegradation of semiconductors of the $A^{II}B^{VI}$ group leads to the fragility of devices based on them [1]. The stability of photoelectric characteristics and degradation resistance of polycrystalline films $A^{II}B^{VI}$ can be increased by adding compounds of group $A^{IV}B^{VI}$, for example PbS. Structures with both CdS [2–4] and PbS [5,6] predominance are of interest.

The purpose of the work is to study heterogeneous film materials based on CdS and PbS components, conventionally designated CdS-PbS, depending on the ratio of components in the finished film and to establish the features of photocurrent changes that occur under the influence of illumination in different spectral ranges.

Film samples with different ratios of CdS and PbS components were produced, obtained by hydrochemical deposition (HCD) [7]. The HCD method does not require the use of complex vacuum technology and high temperatures, which is its advantage over other technologies. CdS-PbS films were deposited onto a glass substrate from a citrate-ammonia reaction mixture containing salts of its two constituent metals and various ligands involved in complex formation. The concentration of an aqueous solution of chemically pure cadmium acetate $Cd(CH_3COO)_2$ varied from 0.06 to 0.12 M, the concentration of lead salt $Pb(CH_3COO)_2$ remained constant (0.04 M). Thiourea N_2H_4CS was used as a chalcogenizer.

The chemical elemental composition of the finished films transferred to a glass substrate was monitored using energy-dispersive analysis on a Tescan Mira II scanning electron microscope (SEM). Also, in the secondary electron mode, the surface morphology, which changes with varying the ratio of the PbS and CdS components, was studied. It was found that in the structures under study, where the concentration of cadmium acetate during synthesis was 0.06−0.08 M, the PbS phase predominates (82−88%). The use of 0.10−0.12 M cadmium acetate in the synthesis leads, accordingly, to an equal phase ratio (1 : 1) and to the predominance of CdS (up to 67%). Figure 1 shows SEM images of the samples surface under study, from which it is clear that when the CdS phase predominates on the surface and in the bulk of the film, multiple nanoscale and submicron PbS precipitates are formed (Figure 1, *a*), which is due to the low solid solubility of PbS in CdS (up to 0.06%). There is a similar picture at equal concentrations of CdS and PbS. In the case of a PbS predominance (Figure 1, *b,c*), almost all CdS is dissolved in PbS (maximum solubility up to 30 mol%) and only single CdS precipitates are observed on the surface of the film of the $Pb_xCd_{1-x}S$ substitutional solid solution.

Using a Shimadzu IRAffinity Fourier-transform spectrometer, the reflection and transmission spectra of the obtained samples were measured in the infrared (IR) range. When analyzing the spectra, the reflection and transmission spectra of laboratory colorless glass onto which the films were deposited were taken into account. Figure 2, *a* shows the reflection spectra of the films under study in a wide IR range from 1 to 30 μm. The transmission spectra were measured in the most relevant wavelength region for these structures, 1−6 μm (Figure 2, *b*). From Figure 2, *a* it follows that films with a PbS predominance are more reflective in the entire range under consideration, and there is a
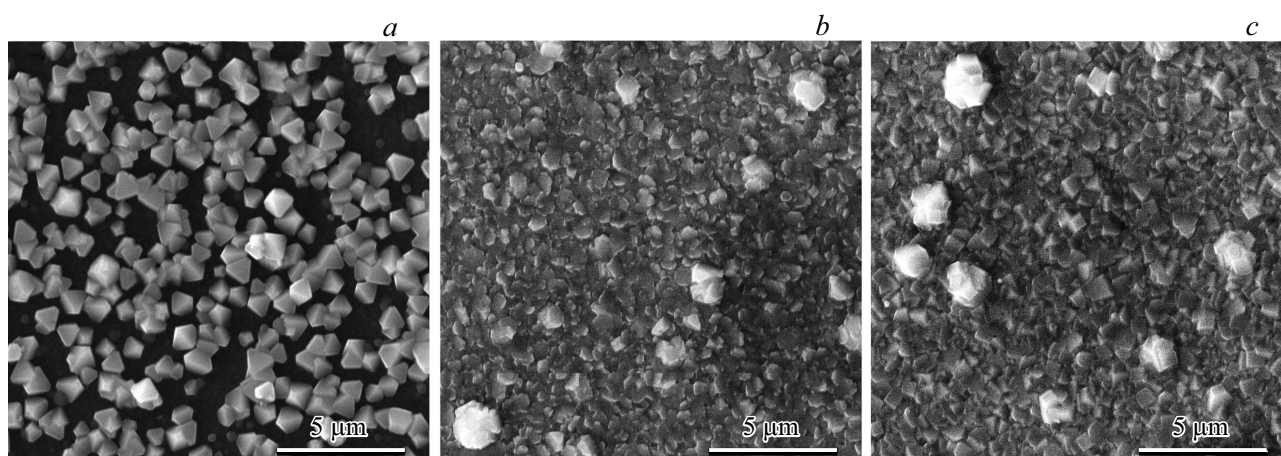
Figure 1. SEM images of the sample surface: a — CdS (67 mol%), PbS (33 mol%); b — CdS (18 mol%), PbS (82 mol%); c — CdS (12 mol%), PbS (88 mol%).

interference pattern in the spectra. The CdS-dominant film demonstrates significant reflectance only in the range from 5 to 8 μm and its spectra are non-interferential. In many respects, the reflection spectrum in the IR region for a film with a predominance of CdS is due to reflection from the glass substrate, but in the mid-IR range there are lines due to reflection from the photosensitive heterophase film CdS-PbS, which coincides with the data of the article [8].

Minima in the optical transmission spectra (Figure 2, b) in the IR region are associated with various types of absorption: proper absorption of PbS takes place at a wavelength of $3.1 \pm 0.3\,\mu$m (depending on the size of the crystallite), the formation of solid solutions based on it in a fairly wide range it gives a wide absorption band in the middle and near IR ranges. For a sample with a predominance of CdS, absorption in the near-IR range (up to 1.8 μm) is due to the formation of solid solutions based on this wide-band semiconductor with PbS. The appearance of local minima in the transmission spectrum can be caused by absorption in nanoscale precipitates of PbS-based solid solutions, formed due to the very low solubility of PbS in CdS.

Photovoltaic characteristics were studied on a PM-5 probe station (Cascade Microtech) using an Agilent B1500a semiconductor device analyzer. Current-voltage characteristics (IV-curve) were measured in the dark and under illumination in the transverse photoconductivity mode. Illumination was carried out using a white LED based on a phosphor (peak wavelength 465 nm) and an IR LED ($\lambda = 940 \pm 50$ nm) at the same radiation intensity (≈ 3 mW/SR). Current-voltage characteristics for each sample were measured in the following sequence: 1) measurement of IV-curve of the sample in the dark; 2) measurement of IV-curve under IR illumination; 3) measurement of IV-curve when irradiated with light in the visible range.
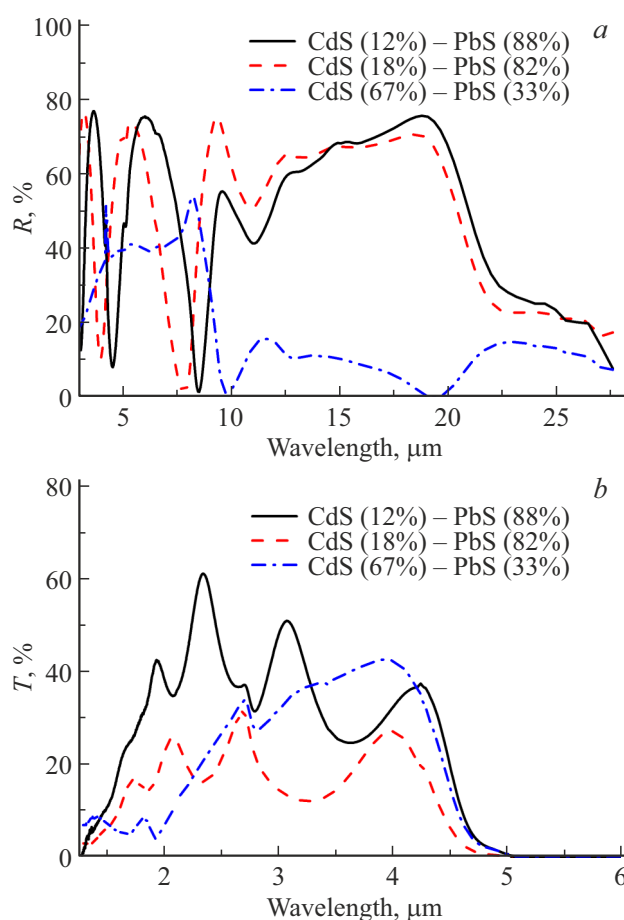
Figure 2. Reflection (a) and transmission (b) spectra in the IR range for film samples on a glass substrate.

Figure 3 shows typical sets of IV-curves under different illumination conditions for heterophase samples with a predominance of the CdS or PbS phase. For samples with a high content of the PbS phase, there is a certain kind of
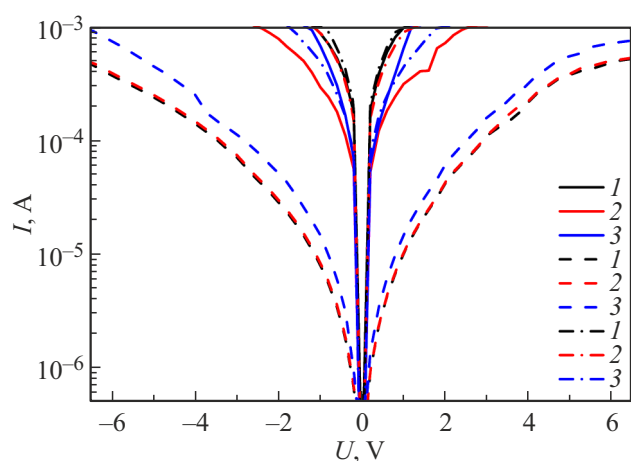
Figure 3. IV-curve of the samples: solid lines — CdS (18 mol%), PbS (82 mol%); dash-dot lines — CdS (12 mol%), PbS (88 mol%); dotted lines — CdS (67 mol%), PbS (33 mol%); *1* — in the dark, *2* — under IR illumination, *3* — when irradiated with light in the visible range. (The colored version of the figure is available on-line).

quenching of intrinsic photoconductivity, which manifests itself in a decrease in the photocurrent relative to the dark current when irradiated with light from the visible range after IR irradiation. Meanwhile, for samples with a predominance of the CdS phase, the photocurrent exceeds the „dark" current in accordance with the „classical" photoconductivity model.

In addition, for samples with a high content of PbS, the kinetic dependences of the current showed that even after short-term illumination for 10 min simultaneously with IR and white light „dark" resistance decreases by $3-5\%$ and slowly relaxes to the initial value during few hours. The samples, which are a CdS film with numerous PbS precipitates, demonstrated high stability over time of the dark current after a similar illumination.

The observed differences in changes in currents upon illumination with light from the IR and visible ranges for two groups of samples of the CdS-PbS type can be explained by the simultaneous use of the two-level Rose model [9] and different types of photochemical reactions (PCR) in these samples [10] associated with the recharging of energy levels under IR illumination and the drift of mobile defects.

The Rose model is usually used to explain IR quenching in semiconductors. The model assumes the presence of two types of energy levels in the band gap — attachment levels (with a large capture cross section for electrons) and a recombination center, in which the capture cross sections for electrons and holes are the same. At a certain photon energy, it is assumed that electrons will be captured by attachment energy levels, and free holes will be captured by recombination levels, which will lead to the effect of photoconductivity quenching. In the films we studied with a predominance of PbS, dissolved divalent Cd forms „deep" acceptor levels in the PbS band gap,

which, due to the small width of the PbS band gap, are easily recharged by IR radiation. Since the capture cross section for electrons and holes depends largely on the level charge, dissolved Cd atoms in PbS can provide the two types of levels required to realize IR quenching according to the Rose model. Since in the dependences of Figure 3 for samples with a predominance of the PbS phase there is a steady decrease in the photocurrent below the dark values even after turning off the IR radiation, only under the influence of light in the visible range, this indicates the formation of stable associates of donors and acceptors under the influence of IR radiation leading to the formation of additional recombination levels. The reversible nature of these changes, recorded in the kinetic dependences of the current, also confirms this assumption.

In samples with a predominance of CdS, a large number of additional levels in the band gap are not formed due to the very low solubility of Pb, but nanoscale inclusions of the narrow-gap PbS component are formed, which are defect getters. Point defects from the CdS phase drift in the field of the heterojunction at the boundaries of the CdS and PbS phases into the narrow-gap phase and remain in it due to the small diffusion constant and the presence of an energy barrier at the phase boundary. As was described in works [2,3], this leads to a significant stabilization of the photovoltaic characteristics of these films.

Thus, it has been shown that depending on the predominance of CdS or PbS in a heterogeneous semiconductor, not only does the spectral range of photosensitivity change, which is predictable, but also the surface morphology significantly changes, with the structural features of which changes in the optical characteristics and the nature of the change in the photoelectric characteristics of heterogeneous systems are completely correlated. An increase in the stability of photovoltaic characteristics is demonstrated only by samples with a predominance of CdS, and with a predominance of PbS, there are photoquenching and slow relaxation of the dark current after turning off the illumination.

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Conflict of interest

The authors declare that they have no conflict of interest.

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