Fabrication of nanocomposite film coatings to increase the radiation hardness of CdS-like photoconductors

P G Kharitonova, S V Stetsyura, A V Kozlowski and I V Malyar
Department of Nano- and Biomedical Technologies, Saratov State University, Saratov 410012, Russia
E-mail: haritonovapg@gmail.com

Abstract. We demonstrated that the size and the distribution density of lead-containing inclusions in the topmost layer deposited on CdS depend on the pH of a Pb(NO₃)₂ solution, which is used to fabricate a coating for CdS by Langmuir-Blodgett technology. The formation of a nanostructured lead-containing film was controlled by Brewster angle microscopy and scanning electron microscopy. The best parameters of the photosensitivity and radiation hardness of a CdS semiconductor with a nanostructured lead-containing surface layer were achieved using a solution of pH ≈ 8 and a Pb(NO₃)₂ concentration of 10⁻³ mol/L. We performed modeling of the optimal size and location of lead-containing clusters.

1. Introduction
At present, significant attention is paid to the study of the properties of film materials based on CdS [1-5]. CdS is widely used in various structures for optoelectronics due to its highly-sensitivity to visible radiation. A drawback of this wide-gap semiconductor is its low hardness to ionizing radiation, in particular, to β-radiation. Previously [6], we proposed to prepare microinclusions, which are non-photosensitive in the optical range, as a sink of point defects generated under irradiation, which increases the radiation hardness of CdS and decreases its photodegradation. We demonstrated that a PbS narrow-gap semiconductor is well fitted for this purpose. The nanodimensional inclusions of narrow-gap PbS were fabricated in the bulk of the CdS semiconductor using the method of thermal evaporation [7]. However, it also slightly reduces the CdS photosensitivity due to an increase in the recombination flux of photogenerated charge carriers into the narrow-gap phase and a decrease in the volume of the photosensitive phase. Therefore, we propose to fabricate getter sinks of point defects only in the topmost layer region of CdS, where radiation defects are formed and radiation-induced diffusion occurs, to provide the radiation hardness to electrons of low and medium energies.

Thus, the aim of this work is modeling the optimal heterophase structure, which provides an increased radiation hardness and the photosensitivity of a submicron thickness CdS film. We also intended to determine the technological mode for realization of this modification of the topmost CdS layer.

2. Modeling of a structure providing the radiation hardness
We obtained experimentally the dependence of the concentration of Pb atoms on their depth in a CdS sample with an enhanced radiation hardness by the method of secondary ion mass spectrometry. The radiation hardness was tested under irradiation of CdS by electrons of low and medium energies. We applied the theory of precipitation in materials with limited solubility of components and estimated the
occurrence depth of PbS inclusions, their minimum radius, which is less than 10 nm, and their surface and bulk distribution density in CdS to achieve effective gettering of point defects and to provide the same photosensitivity (figure 1). The main type of radiation defects in CdS is an interstitial ion of Cd$^+$. Cd$^+$ is gettered in PbS due to the potential relief of the CdS - PbS heterophase semiconductor and the difference in the coefficients of radiation-induced diffusion of Cd$^+$ in CdS ($D = 10^{-14}$ m$^2$/s) and in PbS ($D = 10^{-29}$ m$^2$/s). We carried out a further calculation for a CdS sample with a thickness of up to 2 μm, in which PbS clusters were located only on a surface with a density of $2.5 \times 10^7$ cm$^{-2}$. We calculated that all the point defects formed in a CdS film under irradiation by electrons with an energy of 20 keV will pass a distance of 2 μm in less than 0.08 seconds. The radiation defects of Cd$^+$ will be captured by PbS when they are in the field of narrow-gap inclusions. The defect will move at a rate of $\sim 0.17 \times 10^{-19}$ m/s in the PbS phase and thus be in the narrow-gap phase for a long time. The amount of Cd$^+$ in PbS can be up to 26 wt % of the phase mass. This circumstance makes it possible to capture all point radiation defects (Cd$^+$) in the PbS phase with the calculated values of the distribution density and the size of the PbS inclusions.

![Figure 1](image.png)

**Figure 1.** Calculated dependences of the average number of particles in narrow-gap lead-containing inclusions (a) and the average radius of these inclusions (b) on the depth of inclusions.

Thus, we demonstrated that nanodimensional sinks on the topmost layer of CdS films are sufficient to increase the radiation hardness of micron CdS films by an order of magnitude.

3. The results of the technological experiment and radiation test

Modification of the topmost layer of a submicron thickness CdS film is achieved as a result of diffusion of a slightly soluble component from a limited source (e.g., a nanodimensional layer of lead arachinate). This layer can be obtained by Langmuir-Blodgett (LB) technology. In this case, the size of the lead-containing inclusions and the distribution density on the surface of CdS depend on the preparation conditions of LB films [8] (in particular, on the pH of the subphase where LB films were formed [9]).

We prepared film coatings for CdS by LB technology using a solution of Pb(NO$_3$)$_2$ with a concentration of $c = 10^{-3}$ mol/L at different pH values (from 4.0 to 10.2) as a subphase. Arachic acid was used as a surface-active material. The formation of lead-containing particles in the water subphase was controlled by the method of dynamic light scattering which allows monitoring of electrokinetic potential changes and a diameter of lead-containing particles depending on the pH of the subphase (figure 2).
Figure 2. Experimental dependences of the $\zeta$-potential (a) and the size (b) of lead-containing particles on the pH of the solution.

The electrokinetic zeta potential ($\zeta$ – potential) arises at the slip boundary between the adsorbed and diffuse parts of the double-electric layer of a colloidal particle. It depends on the thickness of the diffuse layer and characterizes the stability of colloidal systems. There is a rapid increase in the radius of the colloidal particle (by 400 times) at values of $\zeta$ - potential of up to 30 mV. There is no obvious increase in the radius of lead-containing particles in the region of relative stability of the solution ($30 \text{ mV} < \zeta < 50 \text{ mV}$). Some increase in the size of particles (up to pH $\approx 8$) is explained by the addition of OH groups and the formation of lead hydroxo complexes. At higher pH, a decrease in the $\zeta$-potential indicates compression of the diffuse layer around the nanoparticle due to the transition of counter-ions from the diffuse layer to the adsorbed one. This circumstance, as well as the compaction of the cluster structure under the formation of polynuclear conglomerates, leads to a decrease in the radius of nanoparticles.

The formation of a nanocomposite film based on an organic matrix and lead-containing inclusions on the surface of the water subphase was monitored by Brewster angle microscopy (figure 3). The structure of the formed coating transferred onto a solid substrate was studied by scanning electron microscopy (SEM) (figure 4).

Figure 3. Images of lead arachinate layers on the water subphase surface, obtained by Brewster angle microscopy: (a) pH = 4.5; (b) pH = 7.8; (c) pH = 10.2.

Figure 4. Backscattered SEM-images of lead arachinate layers on a semiconductor substrate obtained at different pH: (a) pH = 4.5; (b) pH = 7.8; (c) pH = 10.2.
Samples of CdS were dried at 100°C for 30 minutes after application of a monolayer coating of lead arachinate. Further, we measured the ratio of the sample resistance in the dark to the resistance under illumination of 1000 lx before \( (K_1) \) and after \( (K_2) \) irradiation by accelerated electrons with an energy of 20 keV. From table 1 it can be seen that the minimum relative change of resistance under illumination after electron irradiation \( (\delta K) \) is observed for CdS with a lead-containing coating when using a solution with pH = 7.8.

| Sample          | pH of solution | \( K_1 \)  | \( K_2 \)  | Relative change \( \delta K \), % |
|-----------------|----------------|------------|------------|---------------------------------|
| Uncoated CdS    | -              | 5010       | 450        | 91                              |
| CdS+ArhPb       | 4.5            | 4790       | 3257       | 32                              |
| CdS+ArhPb       | 7.8            | 4810       | 4589       | 5                               |
| CdS+ArhPb       | 10.2           | 4070       | 3744       | 8                               |

4. Conclusion
The present experiments with CdS with a monolayer coating based on lead arachinate and lead-containing clusters demonstrate the stability of its photoelectric characteristics under radiation by electrons of medium energies (20 keV), which confirmed the efficiency of the developed technology. The best parameters of the photosensitivity and radiation hardness of a CdS semiconductor with a nanostructured lead-containing coating were achieved using a solution of pH ≈ 8 and a Pb(NO₃)₂ concentration of 10⁻³ mol/L.

Acknowledgments
The work was supported by the Russian Foundation for Basic Research (№ 16-08-00524_a).

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