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Thermosensitization of nanostructured PbSe films

The mode and conditions of thermal sensitization in the temperature range 648–698K lead selenide films deposited from ethylendiamine acetate system were determined. The effect of heat treatment on the morphology and properties of photosensitive chemically deposited films of PbSe was showed. It is concluded that the results obtained by hydrochemical synthesis of nanostructed highly sensitive to infrared range radiation layer of lead selenide provide performance on the level of best foreign analogues.

Introduction

Lead selenide is a semiconductor material most in demand for the creation of IR detectors for spectral range of 2–5 mkm[1,2]. One of the promising methods of forming of PbSe thin layers with high functional properties is hydrochemical deposition. This method is simple to implement, has a wide range of technological capabilities helping, by having in its base a colloid-chemical stage, to create nanostructured semiconductor layers[3,4].

The present study is devoted to the study of the process of thermosensitization of hydrochemically deposited PbSe films for providing high sensitivity for IR radiation.

The experimental part

Hydrochemical synthesis of lead selenide layers was carried out in a fixed-type reactor at temperature range of 308–343 K at the process time of 40–60 minutes. Degreased pyroceramics plates ST-150 were used as substrates.

Preparation of highly sensitive to IR radiation PbSe films requires a manda-

One of the key questions in obtaining highly-functional PbSe films is the question of formulating of the reactionary bath tank. From the point of view of producing films of a certain thickness and structure, the choice of complexing agents for lead ions is important; this role was performed by ethylendiamine $C_2H_4N_2H_4$ and ammonium acetate NH_4CH_3COO. As an antioxidant for unstable in air aqueous solutions of selen carbamide CSeN2H4, sodium sulfite Na_2SO_3 was used. For increasing of the sensitivity of the lead selenide films to infrared radiation, ammonium iodide NH_4I was additionally introduced into the reaction mixture.

tory operation of sensitization, for which annealing in air is used. Heating leads to the recrystallization of layers and oxygen phased additions, in particular, to the formation of oxygen-containing impurity phases such as PbO, $PbSeO_3$. Their presence in the layer helps to optimize the carrier density and increase the value of photo response. For this work, annealing of the deposited films was carried out at temperature range 648–698 K.

The crystal structure of the deposited lead selenide films was investigated in details using X-ray diffraction. Radiographs were obtained on a diffractometer "DRON-4" in the angular range 2ϑ = 20–90° in step-scan mode, $\Delta\theta$ = 0.03 degrees. Copper radiation using pyrolytic graphite as a monochromator for distinguishing CuKα doublet from the continuous spectrum was used.

Electron microscopic images of PbSe layers are made with a scanning electron microscope JSM-6390.

The measurement of photoresponse of synthesized films was carried out on measuring stand K.54.410 after the electrochemical deposition of paired nickel contacts. The blackbody 573 K was used as a radiation source, providing the irradiated samples at 9×10^{-5} Vt.sm^{-2} and at a modulation frequency of radiation in the optical flow 1200Hz. The bias voltage is set at 6 V/mm.

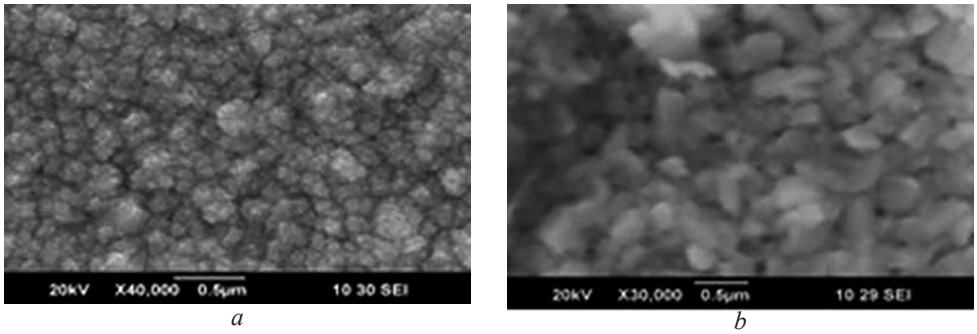
Results and discussion

Using X-ray diffraction, it was found that annealing leads to some increase in constant of the PbSe crystal-lattice (structure B1) from a = 0.61185 nm for the freshly precipitated layers to a = 0.61606 nm for the heat-treated at 678 K. This may be due to the process of film recrystallization and the ordering of their structure.

The results of electron microscopy studies of PbSe layers are shown in Fig. 1. It draws attention that freshly precipitated PbSE layer (Fig. 1a) is formed of spherical particles with prevailing globule sizes of 80–200 nm, which, in turn, are composed of spherical units of ~ 25–40 nm in diameter.

Thus, obtained hydrochemical PbSe deposited layers are nanostructured in their architecture.

It can be concluded that formation and growth of films of lead selenide from aqueous solutions proceeds according to cluster-cluster aggregation, involving colloid chemical processes happening not



a *b*

Fig. 1. Electron microscopic images of freshly precipitated (*a*) and annealed at a temperature of 678 K (*b*) PbSe films. Annealing time is 10 minutes

only on the substrate surface but also in volume of the reaction mixture.

Heat treatment significantly alters films morphology. As a result of recrystallization, an increase in pri-mary nanoscale aggregates up to 300–600 nm with changing their crystallographic form occurs (see Fig. 1b).

We shall note that the size of the films microcrystals from the results of electron microscopy studies are in good agreement with the estimate of the average size of the coherent scattering films regions, calculated according to the Debye-Sherrer formula from X-ray data from the studies.

Fig. 2 shows the dependence of the photo-response of PbSe films from the time they were annealed at temperatures of 648, 673 and 698 K. Dependencies have pronounced maximum of response, which with increasing temperature shifts toward shorter annealing. Annealing at 698 K leads apparently to a sharp increase in the rate of oxidation of lead selenide and characterized by narrow time ranges of rated maximum photoresponse. On the other hand, it is clear that at an annealing temperature of 648 K, the process of sensitization is significantly lengthened, not allowing achieving a high volt-watt sensitivity of the films. It can be concluded that the magnitude of photoresponse of layers is the result of interconnected time-temperature effects on the structure and composition of impurity. To ensure high values of photoresponse, it is necessary to select conditions to achieve a certain degree of recrystallization and the level of oxygenation of the layer. It is found that the decrease in crystallite sizes, which form PbSe films, contributes to a significant increase in the level of its photoresponse.

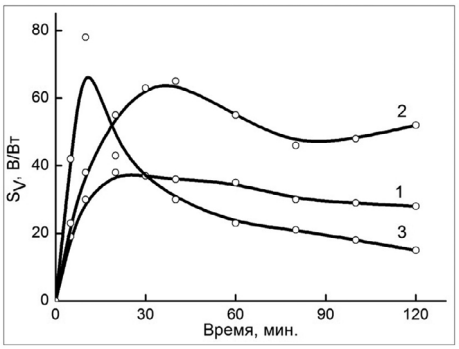


Fig. 2. Dependence of the current-watt sensitivity of the PbSe films on duration of annealing at 648 K (1), 673 (2), 698 K (3)

Thus, the heat treatment of hydrochemically in air deposited nanostructured PbSe films by choosing of mode and process parameters, provides the possibility of obtaining layers with high values of the photoresponse to IR radiation, including to the level typical of the best foreign models.

1. Butkevich V. G., Bochkov V. D., Globus E. R., Appliead Physics. 2001; 6:66.
2. Bode D. E. Detectors on basic Ph-salts. 1968; 3:299–327.
3. Markov V. F., Maskaeva L. N., Ivanov P. N. Hydrochemical precipitation of film sulfide metals: modelling and experiment. Ekaterinburg: UrO RAN:2006, 216.
4. Markov V. F., Maskaeva L. N., Loshrareva L. D., Uimin S. I., Kitaev G. A., $Pb_{1-x}Sn_xSe$ Substitutional solid solution prepared by coprecipitation from aqueos solution.Inoranic materials. 1997; 33(6) : 665.