The influence of mobile impurities on photoelectric properties of PbSe-based multiphase photosensitive structures

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Abstract. The PbSe-based photoelectric sensor technology is considered. The polycrystalline PbSe films are used for the production. The influence of mobile impurities in a material on the mechanism of the photovoltaic effect is revealed and investigated. The experimental results of investigation of the photovoltaic effect are discussed.

1. Introduction.

Fire-fighting measures are very important for fire safety of all technological processes. Despite the significant progress in fire-fighting systems, fires stay a serious problem of modern society because they continue to claim lives and cause immense damage. So timely fire detection is essential for efficient fire fighting. The number of factories which use highly flammable and explosive materials increases. Thereby the requirements to a technological process monitoring were strengthened.

Nowadays there are several types of flame detectors which are widely used in fire monitoring systems. Among them are thermal, smoke, gas and optical flame detectors. Each of them responds to a special fire signature (heat, smoke, gas or optical radiation). Operating experience has demonstrated that optical systems were the most efficient devices for fire safety control of technological processes. Optical flame detectors respond to flame optical radiation, allowing detection of fire in its early stage. Optical flame detectors also can be used in large halls and outdoors. The main disadvantage of such systems is probability of false alarms caused by natural and industrial interferences. The interference power can be several orders of magnitude greater than the flame radiation power [1]. So the optical flame detectors must respond to some specific radiation properties of flame. In modern optical systems two fire detection methods are used: frequency and spectral selection of registered signal [1, 2].

The frequency selection means the detection of low-frequency oscillations of radiation intensity (from 1 to 20 Hz), caused by the turbulent nature of fire. This method has a number of disadvantages. Among them are low interference protection and high response rate of the optical detector (1-10 s). Moreover the frequency selection is useless for smoldering fire detection [1, 2].

The experimental data shows that the spectral selection is more efficient for flame detection. This method allows detecting the definite spectral bands in registered signal. There are the spectral band of hot water vapor with spectral characteristic peak at 2.9 μm and the spectral band of hot carbon dioxide CO$_2$ with peak at 4.4 μm in the flame spectrum (figure 1). So, several photoelectric sensors should be used for the spectral selection. Some of them detect the spectral bands of water vapor and CO$_2$. And the others are used for monitoring of optical interference radiation in the range 0.9-1.1 μm. This method allows us to eliminate the disadvantages of the frequency selection and to solve the problem more efficiently.
To improve the fire-fighting optical systems based on the spectral selection it is necessary to increase the spectral sensitivity, response rate and operational reliability of integrated photodetectors.

The use of the photovoltaic infrared sensors based on polycrystalline PbSe films and PbSe–CdSe solid solutions is a promising approach. The spectral sensitivity of these photoelectric sensors in the range 1.5-4.7 μm is considered to be satisfactory. These photovoltaic infrared sensors can operate in temperature range from -60°C to +60°C without cooling [1]. The compositional change of semiconductor material allows us to control the spectral characteristics of the photoelectric sensors. So they can detect radiation from one or several types of fires or from interference sources [2].

In this paper we present the experimental results of investigation of mechanism of the photovoltaic effect in photoelectric sensors based on PbSe. This data enables to improve properties of developed photoelectric sensors.

2. The photovoltaic PbSe based sensor technology.
A new photovoltaic sensor technology is developed in research laboratory of JSC “NII Giricond”. We have used the thin-film polycrystalline structures based on A₄B₆ materials and A₄B₆-A₂B₆ solid solutions. The main materials for polycrystalline structures are PbSe doping with group V impurities (e. g. Bi) and solid solutions of PbSe and CdSe. Conductivity of these materials is near to intrinsic (this is achieved by the doping with group V atoms). We can change the band gap of the material directionally between 0.2 and 0.6 eV by addition of CdSe to PbSe that allows us to control the spectral characteristics of the photoelectric sensors. The manufacturing technology of different configurations photoresistors and photovoltaic cells with the use of these polycrystalline structures is successfully used in JSC “NII Giricond” [4-6].

The polycrystalline films are created by vacuum thermal evaporation of basic p-type semiconductor material followed by its deposition onto a dielectric glass substrate [1, 5, 7]. High temperature heat treatment (T>300°C) causes the collective recrystallizing of crystallites, their dynamic oxidation and interaction of these oxides with the substrate material. As result the photosensitive grid-type structure covered by oxide-glassy substance arises [7]. Next the Au and In contacts are printed on the surface of photosensitive layer by photolithography. An electric field arises in the clearance between In and PbSe because of electronegativity difference between them. The electric field causes the enhancement of this area by electrons. The energy bands bend downward. N-type area arises. The p-n-junction is formed at the boundary between areas with different types of conductivity (base area).
p-n-junction is necessary for design of self-powered photodetectors operating in photovoltaic mode. The additional heat treatment (200-300°C) boosts the process described above.

3. The experimental technique and the results.
The mechanism of the photovoltaic effect in developed photoelectric sensors has not been fully investigated. It has been previously assumed that the barrier structure formation was caused by the diffusion of indium atoms from the indium contacts to the photosensitive layer during thermal treatment. Based on the received data it can be expected that the photovoltaic effect was induced by the migration of the mobile impurities from the glass substance surrounding PbSe crystallites (mostly Na⁺ ions) to the photoelectric layer. The ion mobility increases with temperature. There is a positive charge accumulation on the surface of the crystallites. The Fermi level of PbSe grain is gradually shifted toward conduction band when the crystallites are sufficiently small (dimensions are much smaller than the shielding length \( l_S = 10^{-4} \text{ to } 10^{-5} \) sm). As a result there is conductivity type conversion from p to n [8].

A scheme of the experimental setup for the investigation of the impurity migration is presented in figure 2.

![Figure 2](image)

**Figure 2.** A scheme of the experimental setup: 1 – photoelectric sensor (photoresistor or photovoltaic cell); 2 – thermostat; 3 – voltage power supply; 4 – switches for changing direction of the electric field; 5 – the research mode switch; 6 – multimeter GDM 354 A; 7 – the device for automatic measurement of volt-ampere characteristics; 8 – PC.

Na⁺ ions have a positive charge. So we can control its migration by the electric field. The direction of the electric field can be changed by switches 4. The voltage U=250 V from power supply 3 was applied to the investigated photoelectric sensor. The photoelectric sensor was also affected by the temperatures T=120-150°C (the sensor was placed into the thermostat 2).

The investigated photoelectric sensor based on Pb₀.₉₆Cd₀.₀₄Se (photoresistor) is presented in figure 3. The p-n-junction doesn’t arise in the photosensitive layer of this sensor because there is no In electrode and this sensor was not affected by additional heat treatment. But there are mobile impurities in the substrate. To investigate the impurity migration we affected the photoresistor by electric field and temperature and measured the resistance of it (see a scheme of the experimental setup in figure 2).
The photoresistor was affected by electric field in the following way: a positive voltage from power supply 3 was applied to substrate, a negative voltage to golden (Au) electrode. Then the direction of the electric field was reversed by the switches 4. The dependencies of the photosensitive layer resistance upon time are presented in figure 4.

Figure 4. Time dependence of the photosensitive layer resistance: a) a positive voltage is applied to substrate, a negative voltage to golden electrode; b) a negative voltage on substrate, a positive voltage to golden electrode.

Figure 4a shows the increase of the photosensitive layer resistance until it reaches a maximum. Then resistance decreases and reaches values lower than initial. We detected a conductivity type conversion of the photosensitive layer from p to n with use of hot-probe method. Then the direction of the electric field was reversed (switches 4 in figure 2). In figure 4b we can also see the increase of the resistance to a maximum. But its value is less than in figure 4a. Then the resistance decreases to a fixed value. A conductivity type changes from n to p after reaching a maximum. The resistance curve in figure 4b is shallower than in figure 4a.

We explain this process as a result of the migration of the positive charge Na\(^+\) ions moved with the electric field from the substrate to the photosensitive layer. This causes the increase of the photosensitive layer resistance. A conductivity type of the material changes when the ion concentration in the photosensitive layer reaches some value. Then the photosensitive layer decreases with enhancement of the Na\(^+\) concentration because of the increase of the electron concentration. We observe an opposite effect when the direction of the electric field was reversed. There is outflow of positive ions Na\(^+\) from the photosensitive layer, a conductivity type of the layer changes again. The final state of the photoresistor is similar to initial. The obtained results show high mobility of impurities in the developed photoelectric sensor.

The investigated photoelectric cell based on Pb\(_{0.96}\)Cd\(_{0.04}\)Se is presented in figure 5 (top view). The p-n-junction was formed in the photosensitive layer as a result of an additional heat treatment. The comb structure of the electrodes was developed to expand the junction plane.
The designed photoelectric cell was placed in the thermostat (see figure 2) where it was affected by the electric field for 40 minutes. The electric field was created by a voltage applied to the photoelectric cell (U=250 V). The switch 5 (figure 2) of the experimental setup was switched to a developed device for automatic measurement of volt-ampere characteristics based on a 8-channel ADC. The data from the device was processed by PC. The results of measurement are presented in figure 6.

![Figure 6. The volt-ampere characteristic of the photovoltaic cell (T=150°C). Graphs 1, 2, 3 correspond to the following voltage values and electric field polarity: 0, +250, -250 V.](image)

The results showed that there is outflow of positive ions Na\(^+\) both from base area and electrode (In) sheath after applying a positive voltage to the photosensitive layer. Thereby the base area resistance decreases. The volt-ampere characteristic becomes practically linear (graph 2). It means that the p-n-junction disappears. There is enhancement of base area and electrode sheath by positive ions after applying a negative voltage to the photosensitive layer (graph 3). The base area resistance increases; the slope of the volt-ampere characteristic decreases. The probability of the reverse conductivity type conversion indicates that diffusion of indium atoms has no dominant role in process of conductivity type conversion of electrode sheath of the photosensitive layer.

Experimental data also indicates that the Fermi level of PbSe grain is shifted by the positive ions Na\(^+\) accumulated near the boundary between grain and dielectric glass substance. Thereby the photosensitive layer resistance increases. Positive charge at the grain boundary increases and this causes a conductivity type conversion. The p-n-junction is formed at the boundary between areas with different types of conductivity.
4. Conclusion
The results obtained in our study indicate that the mechanism of the photovoltaic effect is a result of the migration of the mobile impurities. This enables to improve properties of developed photoelectric sensors by control of the migration of the mobile impurities. But it is also important to determine the configuration of p-n-junction arising in the photosensitive layer and its localization near the In electrode. The solution of the problems will be the goal of our further studies.

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