Preparation of PbSeO₃ as a new material, sensitive to the electromagnetic radiation in UV range

V V Tomaev[1], V D Smolyaninov[2], T V Stoyanova[2] and S V Egorov[2,3]

[1] Institute of Chemistry, Saint-Petersburg State University, Saint-Petersburg, 198504, Russia

[2] Department of General and Applied Physics, National Mineral Resources University (Mining University), Saint-Petersburg, 199106, Russia

[3] Ioffe Physical-Technical Institute, Saint-Petersburg, 194021, Russia

Abstract. The new technology of the formation of photoresistive structures sensitive in ultraviolet range of electromagnetic spectrum based on lead selenide and lead selenite composite is discussed. Studies of photosensitivity were carried out using a set of LEDs in the visible and ultraviolet spectral range. Obtained structures show considerable sensitivity in ultraviolet and blue range of radiation, meanwhile that in red and yellow region of light turned to be small. The structures were formed by oxidation of PbSe crystals. Diffusion of the oxygen through the surface layer of PbSe was suggested to be a key mechanism of oxidation. Oxidation kinetics were studied by means of roentgen lines chemical shift and roentgen diffraction.

1. Introduction

The recent years reveal a steady growth of interest aimed at the materials sensitive to ultraviolet (UV) radiation. The reason is not only new scientific results but also increasing need in devices in industry, medicine, ecology and other fields of human activity.

In the last 10 – 15 years the leading scientific centers actively develop semiconducting UV light emitting diodes (LEDs) and photodiodes (PDs) based on AlGaN nanoheterostructures, with a shortest wavelength emitted 210 nm [1], [2]. One can produce detectors of UV radiation as photoresistors, photodiodes based upon p-n transitions, p-i-n structures and Shottky diodes, field transistors with Shottky barrier and so on. Most often used materials for these purposes are A_3B_5 compounds (GaP, GaN, AlN, SiC) and others, A_2B_6 (zinc chalcogenides, cadmium chalcogenides), ZnO and diamond as well [3] – [10].

2. Materials and methods

Materials which do not reveal sensitivity in the visible range, but reveal it in UV are of special interest. They allow one to improve precision of measurements in UV range. As long as energy gap of lead selenite ($PbSeO_3$) is 3.17 eV [11], one can look forward films on its basis to show high sensitivity in UV range of spectrum and no such a one in the visible range.

This work was aimed at production of $PbSeO_3$ as a new material susceptible in UV range and study of its photosensitivity.

As for all optoelectronic devices, for the receivers of UV radiation, it is important to use direct band-gap semiconductors and the fundamental absorption near the edge of the band-gap [12]. The latter condition implies the presence of a red boundary of signal registration. The boundary wavelength λ_{bound}, exceeding which the registration of radiation is absent, may be determined from the following simple relations at interband transfers:

$$h\nu_{bound} = E_g \qquad \lambda_{bound} = \frac{2\pi\hbar c}{E_g} \qquad \lambda_{bound}(\mu m) = \frac{1.22}{E_g(eV)} \qquad (1)$$

According to the results presented in [12], Table 1 shows the values of the band gap for the individual components (PbSe and PbSeO$_3$) of a two-phase composite lead selenide – lead selenite and the corresponding boundary wavelengths calculated according to relations (1).

Table 1. Wavelength λ_{bound}, corresponding to the beginning of the interband absorption for the semiconductors PbSe and PbSeO$_3$.

Material	Lead selenide (PbSe)	Lead selenite (PbSeO$_3$)
Bandgap width E_g, eV	0.27	3.17
Wavelength λ_{bound}, μm	4.52	0.39

Thus, for the films of a two-phase composite lead selenide – lead selenite under irradiation in a wide optical spectrum of radiation, it is possible to expect the manifestation of the photosensitivity for the PbSe component in the middle infrared region ($\lambda_{bound\ (IR)} = 4.52$ μm) and for the PbSeO$_3$ component in the near ultraviolet region ($\lambda_{bound\ (UV)} = 0.39$ μm).

Films of lead selenide $1 - 2$ μm thick were obtained by vacuum evaporation on a glass substrate. The substrate was rotated during evaporation to improve homogeneity of the film. The subsequent oxidation in a dry air resulted in formation of PbSeO$_3$ phase. It was carried out by means of annealing in electric ovens. Finally compound of two phases PbSe and PbSeO$_3$ was obtained.

The charge state of Se and Pb atoms included in PbSe particles oxidized to a different degree was studied by means of roentgen K-lines chemical shift [13]. Kinetics of oxidation of lead selenide was studied at the temperature equal to 823 K [14]. It was shown that kinetic dependences of oxidation process in lead selenide obtained independently by chemical shift and diffraction corresponds each other quite well. Phase content of reaction products after lead selenide oxidation in a dry air was determined by roentgen diffraction method [15].

Stoichiometrical mass of PbSe was crushed in a gate pounder and subsequently processed in dynamic vacuum to get powder with grains $0.5 - 3$ micrometer size. The crystal structure of the powders was studied by roentgen diffraction using K$_\alpha$ line emitted by Cu electrode in continuous regime under voltage of 25 kV and 20 mA electric current. The angle resolution was $0.001°$. Oxidation kinetics of PbSe powders were studied by means of roentgen lines chemical shift and roentgen diffraction. Study reveals the following: there is no any other phase inside the sample of PbSe, meanwhile at the surface of it a new structure occurs at the room temperature already. This structure is attributed to PbSeO$_3$; volume of the PbSeO$_3$ at the surface increases proportional to the decrease of PbSe. No any other phase was detected in the samples under the temperatures being used.

Diffusion of the oxygen through the surface layer of oxide film towards the boundary crystal oxide is suggested as a main mechanism of oxidation. The target of further processing is to get oxide film of proper thickness via controlling the value of temperature and time of annealing and thus to get composite materials of two phases with proper electro-physical characteristics.

To simplify further analysis, the distinct grain (cross section of it shown at the Figure 1) of PbSe powder thermally processed in dry oxygen atmosphere could be represented as a sphere or as a cube. Figure 2 shows kinetics of new phase of $PbSeO_3$ formation in the grains of PbSe, thermally processed in dry air at $T = 823$ K.
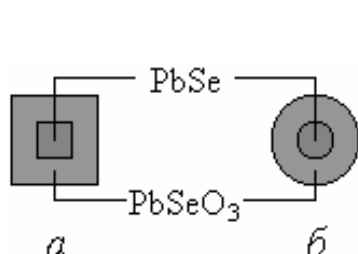

Figure 1. Schematic representation of grain of composite material $(1-x)PbSe \cdot (x)PbSeO_3$ as a cube (a) or a sphere (b).
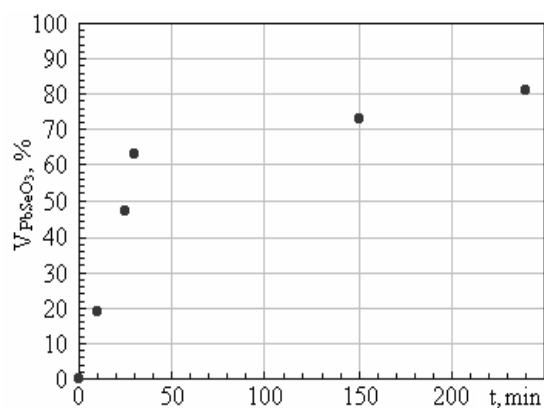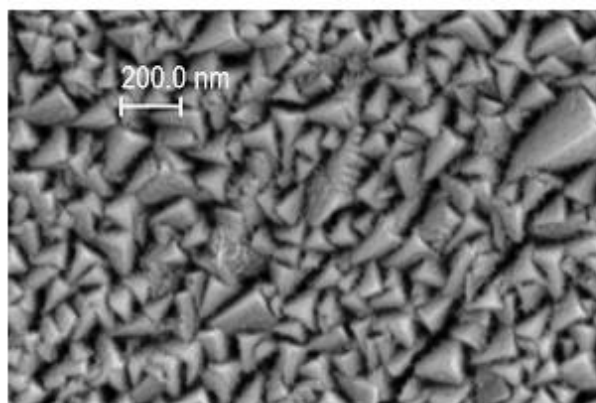
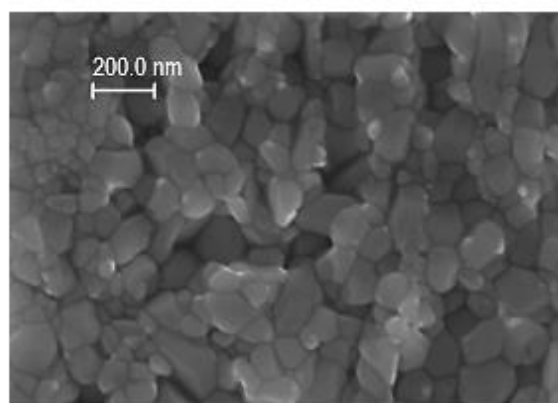**Figure 2.** Quantity of $PbSeO_3$ at the grain surface of PbSe versus time of oxidation.

One can observe two characteristic ranges: range of a rapid increase of oxidized material and a range of reaction saturation, when oxide phase achieves approximately 80 percent, which is in good agreement with roentgen analysis data. Thus, one can control production of PbSe particles inside the dielectric $PbSeO_3$ coating by means of thermal processing in dry air of various time. Time of the processing governs the size of the particles, which might achieve nanometers.

As an initial material one can choose PbSe polycrystalline films, pressed tablets, powder with grains 0.5 – 3 μm size.

Studies of oxidation of PbSe films in dry air were performed at scanning electron microscope Carl Zeiss SUPRA-40VP [16]. Figure 3(a) shows microphotography of the surface of initial PbSe film, produced by evaporation in a vacuum on a glass. It reveals, that surface consists of separate crystals, which have usual for PbSe cubic structure. One can observe at figure 1(a) dominating growth of (100) sides for the crystals of PbSe with average size ~ 150 – 200 nm. Relatively small variation of the size of the crystals implies homogeneous electrophysical and other properties of the films obtained.

(a)

(b)

Figure 3. Microphotographs of the film surface (a) initial PbSe (b) oxidized $(1-x)PbSe \bullet xPbSeO_3$.

Figure 3(b) shows the microphotography of the PbSe surface oxidized at 500 ºC during 60 minutes. Average size of oxidized (1-x)PbSe • xPbSeO$_3$ composite particles is of about 50 – 100 nm.

Taking into account, that at 500ºC after 60 min ~ 80% of the particle volume is oxidized and oxidation occurs at the surface side, one can figure out that core of each of oxidized particle at figure 3b consists of PbSe and is less than 20 nm size while the coating of the particle occupies the rest of the volume and consists of PbSeO$_3$.

In order to obtain a two-phase composite from lead selenide and selenite, the films of lead selenide were oxidized in dry air atmosphere according to the methods presented in [17 – 23]. In order to determine the region of spectral sensitivity of a receiver of optical radiation based on a composite from lead selenide and selenite, it was proposed to use a chosen set of light-emitting diodes as radiating elements, each of which works in a narrow interval of wavelengths in various regions of the spectrum. Working each in its optical interval of wavelengths, they cover the whole spectral range to be studied. At the same time, an important property of UV receivers is the absence of sensitivity to visible radiation [24]. In connection with this, the investigations were carried out in a wavelength range of 315 – 750 nm (from the short-wavelength radiation of UV to visible radiation). With the effect on a photoresistor of radiation with sufficient photon energy for the generation of pairs of mobile charge carriers (electrons and holes), its resistance should decrease. In our studies, such radiation was provided by a set of light-emitting diodes covering a spectral wavelength range of 315 – 780 nm. Four light-emitting diodes for a visible spectrum of radiation and one diode for UV radiation range were used.

In order to determine photosensitivity of a sample one can measure resistance of it under the illumination. A photoreceiver is a semiconductor film resistor based on a composite from lead selenide and selenite, whose resistance can change under the action of radiation. A layer of semiconductor with the silver contacts at the edges is deposited onto a glass wafer. The semiconductor film has a thickness of 2 μm and a surface area of 2 × 3 mm, the area of the silver contact is equal to 1 × 2 mm.

The scheme of a photoresistor circuit is shown in Figure 4. If a photoresistor is connected in series to a voltage source (Figure 4) and is not subjected to irradiation, then a dark current will flow in its circuit:
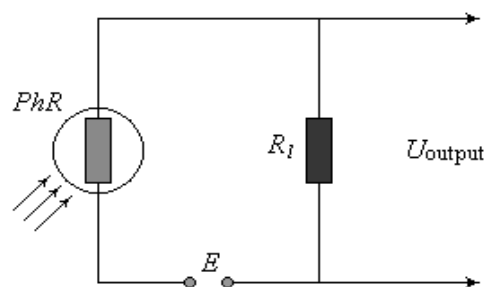

Figure 4. Circuit of the photoresistor

$$I_d = \frac{E}{R_d + R_l} \tag{1}$$

where E is the electromotive force of the supply source; R_d is the value of the electric resistance of the photoresistor in the dark, called dark resistance; and R_l is the resistance of the load. The dark resistance is one of the photoresistor's parameters and has the value ~103 – 105 Ohm. The corresponding current through the photoresistor is called the dark current.

By the illumination of a photoresistor, the energy of the photons is expended to transfer electrons into the conduction band. The number of free electron–hole pairs increases, the resistance of the photoresistor decreases, and a light current, I_i, flows through it:

$$I_i = \frac{E}{R_i + R_l} \qquad (2)$$

R_i is resistance of photoresistor under illumination. The difference between the light and dark currents gives the value of current I_{ph}, which is called the primary photocurrent of conductance:

$$I_{ph} = I_i - I_d \qquad (3)$$

Another important characteristic of a photoresistor is the value of the specific sensitivity, which is determined by the following expression:

$$\frac{\Delta R}{R} = \frac{R_d - R_i}{R_d} \qquad (4)$$

At a certain illumination, the resistance of a photoelement decreases and, hence, the current in the circuit increases, achieving a value sufficient for the operation of the device (it is schematically shown in the form of a load resistance). The useful signal for further amplification or controlling other devices is taken in parallel with R_i.

In our case, the resistance of a photoresistor was determined with the help of measuring bridge AVS-47. The device allows us to measure the resistances of the samples in the range from 2 Ohm to 2 MOhm. The bridge measures the resistance at an alternating current of a frequency of 12.5 Hz. The signal's shape is rectangular pulses. Such a shape allows us to reduce the power released in the studied sample.

3. Experiment and discussion

We have studied resistance of the composite samples $PbSe/PbSeO_3$ illuminated in visible range and UV range of electromagnetic field. We used a set of light emitting diodes as a source of light.
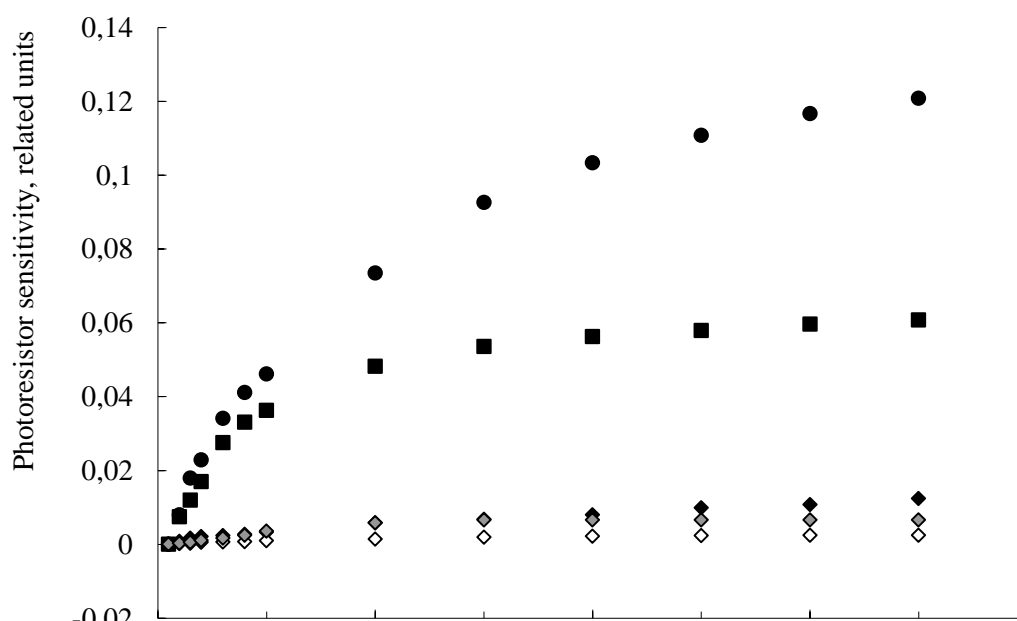

Figure 5. Photosensitivity dependence on LED current.

The diodes were able to emit red, yellow, green and blue light and UV radiation as well. The intensity of diode emission was controlled in accord with its operating current. The samples were illuminated with diodes emitting light of different wavelengths. The sample shows decrease of resistance in UV and blue light region, meanwhile in a red and yellow range of the wavelengths resistance of a sample does not decrease so much. One can calculate sensitivity. This value is shown at the Figure 5.

The energy gap of $PbSeO_3$ is expected to be 3.17 eV [3]. Such energy can be provided by a quantum of radiation with a wavelength about 390 nm, which corresponds to the UV region. We attribute strong susceptibility of resistance under UV light to the layer of $PbSeO_3$ formed over PbSe during the annealing of a sample. Charge carriers are produced by excitation of electrons with a UV energy quanta cross the energy gap. This results into the decrease of resistance.

4. Conclusions

A feature of the proposed material as a new material sensitive to the electromagnetic radiation in UV range is the simplicity of the original film deposition of lead selenide, with its subsequent oxidation to selenite lead and further application of the contact pads on the substrate glass. Photosensitivity of $PbSe/PbSeO_3$ composite films was studied in the visible range and in UV range of spectrum. Maximum sensitivity was observed in the wavelength range 315 − 430 nm. It shows, that $PbSe/PbSeO_3$ demonstrates maximum photosensitivity in UV range of spectrum. Considerable sensitivity of the material exists in blue range, meanwhile it is not sensitive in red and yellow range. It is attributed to the absorption of UV radiation quanta and subsequent excitation of electrons to the conduction band cross the energy gap in $PbSeO_3$ layer formed on surface of PbSe while annealing.

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