Development of epitaxial PbS layers obtaining method for photoelectric transducers

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Abstract. Photoelectric transducers are a semiconductor device that converts photonic energy into electrical energy. This paper describes obtained by the hotwall epitaxy method epitaxial PbS layers technology. Materials, methods, technological parameters of synthesis were selected and substantiated. A theoretical model of the p-n transition has been developed. The calculation of the main parameters has been done. The hotwall epitaxy method was chosen for the synthesis, because it allows to obtain layers with required properties in a single technological cycle with an economical consumption of material. BaF2 was chosen as the substrate, because in this case a smaller difference in the identity periods and the layer and the substrate thermal expansion coefficients is achieved.

1. Introduction
The semiconductor industry is actively developing in the modern world. One of the uses is photonics. Semiconductors have come out on top in terms of breadth of implementation and opportunities for improvement. Such spheres as silicon nanophotonics, glass coatings, two-dimensional crystals for photonics and optoelectronics, and spectral precision lasers are also actively developing [1-3]. This article is devoted to the methods study and the techniques development for obtaining epitaxial layers of photovoltaic cells or photoelectric converters that convert the energy of photons into electricity. At the present stage, converters based on gallium and silicon arsenide are actively used [4]. The development and research of new materials naturally leads to a rethinking of the use of certain structures. Today sulphide-lead, sulphide-cadmium and CIGS (copper, indium, gallium, selenium) structures come to the fore. PbS was chosen because this material has high exponential photosensitivity. Many different photonic devices are based on it. Also, with a decrease in grain size, lead sulfide changes properties due to the size effect, but the structure of the entire material also changes [5, 7].

2. Selection and justification of techniques, materials, technological parameters
Layers of PbS and solid solutions are deposited on substrates from fresh cleavages along the (111) and (100) planes of BaF2 and NaCl single crystals. BaF2 was chosen as the substrate, because in this case a smaller difference in the identity periods and the layer and the substrate thermal expansion coefficients is achieved. The discrepancy between the identity periods between the BaF2 substrate and the epitaxial layers is 4.5-1.3% when the X composition changes from 0 to 1. In turn, the NaCl substrates are hygroscopic, which leads to a violation of the crystal surface perfection. BaF2 (100) substrates are preliminarily subjected to chemical-mechanical polishing in aqueous solutions of...
hydrochloric and sulfuric acids. After polishing, it is necessary to carry out a pre-epitaxial treatment in a mixture of hydrobromic acid and glycerin.

After processing, the surface relief of the BaF2 plates is characterized by a uniform distribution of pits with an average size of 0.2 μm in diameter and a depth of up to 18 nm, the elevations of which form a labyrinthine morphology. Surface roughness Ra averages 12 ± 1 nm.

The hotwall epitaxy method was chosen because it offers all the advantages of vacuum deposition methods. Moreover, this method makes it possible to obtain epitaxial layers of compounds and based on them solid solutions under conditions as close as possible to thermodynamically equilibrium. It is precisely the observance of the equilibrium conditions for the synthesis of epitaxial layers that is more important than the use of oil-free pumping systems requiring ultrahigh vacuum or ensuring a high degree of purification of the initial components [6].

To optimize the conditions for obtaining layers of high structural perfection, the following rules must be observed:

- The synthesis of layers should be carried out at as close as possible the evaporation temperatures of the initial charge and the substrate.
- Avoid re-evaporation of the deposited layer from the substrate, which leads to a deterioration in the quality of the layer surface.
- The substrate temperature must be high enough to ensure the diffusion of absorbed atoms and molecules over the layer surface and recrystallization and annealing of layer defects.

It is necessary to calculate the deposition time in order to set the n- and p-conductivity layers. The deposition time determines the layer thickness. In turn, the layer thickness is determined based on the fact that the mean free path of charge carriers is comparable to the mean free path. This is required in order for the charge carriers to reach the pn junction. It is also necessary to take into account that a situation of diffusion of defects may arise and the p-n junction is blurred. To select the conditions for obtaining, state diagrams are used, but in addition to them, high-quality homogeneous layers with a structure and properties close to a single crystal are required. For this, kinetic studies are used.

It is taken on the basis that the free passage of charge carriers is comparable to the width of the p-n transition.

The kinetic regularities of obtaining layers on BaF2 substrates (Figure 1, (a), (b)) and the dependence of the charge carriers concentration on pressure (Figure 2) should be investigated to select the synthesis conditions that make it possible to obtain sulfide epitaxial layers of high structural perfection [8].

![Figure 1. PbS kinetic regularities.](image-url)
As a result of the experimental data analysis, it was concluded that it is advisable to choose a condensation rate of $2.143 \times 10^{-9}$ m/s and a substrate temperature of 700 K. The evaporation temperature will be 793 K. For 793 K, the pressure $P = 3 \times 10^{-2}$ Pa and $P = 2 \times 10^{-1}$ Pa, with impurity concentration $n = 2.6 \times 10^{18}$ cm$^{-3}$ and $p = 10^{18}$ cm$^{-3}$.

3. Calculation of the parameters of the p-n transition

The calculation of the intrinsic concentration of electrons and holes was made according to the following formulas:

$$N_c = 2 \left( \frac{2 \cdot \pi \cdot m_n \cdot k \cdot T}{h^2} \right)^{3/2} = 1.397 \cdot 10^{23} \text{ cm}^{-3}$$  \hspace{1cm} (1)

$$N_v = 2 \left( \frac{2 \cdot \pi \cdot m_p \cdot k \cdot T}{h^2} \right)^{3/2} = 2.828 \cdot 10^{23} \text{ cm}^{-3}$$  \hspace{1cm} (2)

$$n_i = p_i = \left( N_c \cdot N_v \right)^{1/2} \cdot \exp \left( - \frac{\Delta E}{2 \cdot k \cdot T} \right) = 5.938 \cdot 10^{19} \text{ cm}^{-3}$$  \hspace{1cm} (3)

where $N_c$ – effective number of states in the conduction band reduced to the band bottom, $N_v$ – effective number of states in the valence band reduced to the band ceiling, $m_n$ – effective electron mass, $m_p$ – effective hole mass, $k$ – Boltzmann's constant, $T$ – temperature, $h$ – Planck's constant, $\Delta E$ – value of band gap, $n_i, p_i$ – intrinsic concentration of electrons and holes [9].

The height of the potential barrier is determined as follows:

$$\varphi_0 = k \cdot T \cdot \ln \left( \frac{P \cdot n}{(n_i)^2} \right) = 3.603 \cdot 10^{-20} J$$  \hspace{1cm} (4)

where $n$ – electron concentration, $p$ – hole concentration, $\varphi_0$ – potential barrier height.

The calculated value of the space charge layer thickness refers to an abrupt p-n transition, in which the impurity concentration changes abruptly. The thickness of the space charge layer of the abrupt p-n transition is:

$$d = \left( \frac{2 \cdot \varepsilon \cdot \varepsilon_0 \cdot \varphi_0}{n \cdot q^2} \right)^{1/2} = 1.216 \cdot 10^{-5} \text{ cm}$$  \hspace{1cm} (5)

where $\varepsilon_0$ – permittivity of vacuum, $\varepsilon$ – dielectric constant, $q$ – elementary charge.

Contact-potential difference is:
Performed calculations showed that to obtain a p-n transition under the given conditions, the time $t = 56.783$ s is required. It is necessary to take into account the phenomenon of self-diffusion. To calculate the diffusion process, the equation is solved for the variant of diffusion from a constant source in a body of finite dimensions. As a body of finite dimensions, the space charge region of the p-n transition is considered. It was found that the width of self-diffusion processes is in the range from 0.3 to 0.5 μm.

Therefore, in order not to blur the transition, the thickness of the growing layer must be made larger. The choice of thickness should be in the range from 1.5 to 3 microns (one layer). Taking into account the above conclusions, the thickness should be 2.25 μm.

4. Calculation of volt-ampere characteristics of the p-n junction

Volt-ampere characteristics are shown in Figure 3.

![Figure 3. Volt-ampere characteristic.](image)

These volt-ampere characteristics (Figure 3) are similar to the volt-ampere characteristics of contacts without the rectification effect, but with a resistance that depends on the applied voltage. The nonlinearity of the current-voltage characteristic is due to the phenomena at the point contact between the semiconductor microcrystals. With an increase in both forward and reverse voltages, the resistance of the structure decreases due to the tunneling of charge carriers through surface potential barriers, due to the presence of strong electric fields in them, arising in point contacts between microcrystals. The current-voltage characteristics of the structures remain stable when the electric current is repeatedly passed in the forward and reverse directions. However, the current-voltage characteristics of PbS films with contacts change when a current is passed through them. This is explained by the presence of slow surface states, which are localized on the surfaces of microcrystals and in the oxide layer of intercrystalline gaps. Slow surface states are due to absorbed gas molecules, which are formed during the oxidation and decomposition of PbS during the heat treatment of lead sulfide films.

Development of the topology of p-n junctions manufactured in a single technological cycle, based on epitaxial layers of phases of variable composition

The topology is shown in Figure 4.
Figure 4. Topology of p-, n- junction based on epitaxial layers of phases of variable composition: 1 and 2 are p- and n- type epitaxial layers of electrical conductivity, respectively; 3 - ohmic contact to n-type layers of electrical conductivity; 4 - epitaxial layer used to form a p-n-junction; 5 - ohmic contact to p-type layers of electrical conductivity; 6 - BaF2 substrate.

5. Conclusion
The obtained indicators prove that the chosen hotwall epitaxy method is one of the most suitable for the use of such structures. Secondly, the selected substrate materials and layers for the p-n transition have the required characteristics for use in photovoltaic converters. Thirdly, the main indicators of the p-n transition are calculated, which make it possible to resolve the topology of the photocell.

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