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TECHNOLOGY OF PHOTOSENSITIVE THIN-FILM STRUCTURES CdSe, CdSe:Cd,Cl, CdSe:Cu,Cl WITH LONGITUDINAL PHOTOCONDUCTIVITY

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Abstract
A method for fabricating longitudinally operating cadmium selenide photosensitive films and transparent conductive contacts on SnO2 and CdO is presented. It is shown that photosensitive films with stable and reproducible electrophysical characteristics are obtained using annealing temperatures in air in the presence of CdCl2 of -470°C; and CuCl2 of -300°C.

Keywords: Photosensitive film, CdSe, CdSe:Cd,Cl, CdSe:Cu,Cl, longitudinal photoconductivity, transparent contacts, heat treatment, sensitization kinetics, SnO2 and CdO.

Introduction

Among the A2B6 semiconductors, cadmium selenide is the most sensitive in the visible and near-infrared region of the spectrum. Advances achieved in recent years in the field of technology for the manufacture of polycrystalline films of cadmium selenide operating in the longitudinal photoconductivity mode have led to the creation of a number of photovoltaic devices for micro- and optoelectronics, acoustoelectronics and automation, and nonlinear optics. must be optically transparent for the spectral range of the photosensitive film under study. The range of materials that combine high optical transparency in the visible spectral region, in which AIIVVI group compounds have maximum photosensitivity, is limited. The most common oxide films are SnO2 and CdO [1,2].

The formation of an oxide layer is described by the following main reactions occurring simultaneously [3]:

$2Sn+2O2 \rightarrow 2SnO2$

$$2SnO + 2O_2 \rightarrow 2SnO_2 \quad > 380^{oC}$$
$$2SnO \rightarrow Sn + SnO_2$$

This method produces loose high-resistance layers with a resistance of I05 ÷ of 108 Ohm. Many authors [1,4,5] use the method of pyrolysis of tin chloride for the manufacture of SnO2 layers. The formation reaction of the layer can be represented in the form of the following basic equations:

$SnCl_{2+H2O} \rightarrow SnO+2HCl \uparrow$

$$2SnO + 2O_2 \rightarrow 2SnO_2 \quad > 380^{oC}$$
$$2SnO \rightarrow Sn + SnO_2$$

When used as a source material, the reaction of education can be expressed in the form of

$$SnCl_4 + 2H_2O \rightarrow SnO + 2HCl \uparrow$$
$$SnO_2 + \text{восстановитель} \rightarrow SnO$$
$$2SnO \rightarrow Sn + SnO_2$$

The process of layer formation lasts several minutes. By pyrolysis of the chloride layer, it is possible to obtain layers of SnO2 with electrical resistance from several Ohms to hundreds of thousands of Ohms. From the formation reactions, it can be seen that the film is formed from dioxide, in which conductive impurities SnO and Sn are present [6-8]. Transparency and conductivity of the layer depend on the content of these impurities in the film, which determine the non-stoichiometric composition of the film.

Reactive cathodic sputtering of tin metal is one of the advanced methods of obtaining layers SnO_2. Unlike other methods, cathodic sputtering makes it possible to precipitate films evenly over the thickness due to the use of a source with a large surface, provides high stoichiometrics of the applied layers, and allows you to obtain films of high purity at low temperatures. This process is low-inertia and easily controllable [6, 9-12]. Spraying is carried out in an atmosphere of oxygen mixed with an inert gas. Argon, nitrogen and others are used as an inert gas. The growth rate of the resulting films is significantly influenced by voltage, discharge current, gas composition and pressure, as well as the distance between the electrodes. Depending on these parameters, the method of introduction and the amount of impurities, the electrical and optical properties of the resulting films vary within a wide range.

The authors of the work [13,14] investigated the optical and electrical properties of films SnO_2. In order to change the electrical properties of the film, the authors chose an impurity of antimony, based on the fact that the ionic radius Sn4+ (0,71 Å) is close to the ionic radius Sb (0,62 Å) and antimony has one excess electron relative to tin. They assumed that antimony ions, replacing some atoms Sn in the nodes of the structure SnO_2, form new donor levels in the bandgap, which lead to an increase in electrical conductivity. In work [15,16] when added to 75 ml $SnCl_4$ 96 g SbCl2 transmission and Resistivity of the film SnO_2 were 80% and 50 ohms, respectively · cm.

In [17,18], the effect of antimony impurity on the electrical conductivity of the film was investigated SnO_2. Introduction up to 0.5 wt. % SbCl2 slightly increases the electrical conductivity of the film, and the light transmission of the layers remains almost unchanged.

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With the increase in the number of additives SbCl3 up to 2 weight. % the conductivity of the layers increases, but the light decreases slightly

A $T \approx 55\%$ similar result was obtained in [6], where it is shown that when using pure tin dichloride, it is impossible to obtain low-resistance layers of SnO2. When adding SbCl3 to SnCl2, it is possible to control the electrical and optical properties of tin dioxide films.

The purpose of this work is to improve the technology for obtaining CdSe, CdSe:Cd,Cl, CdSe:Cu,Cl films with longitudinal photopenetration. At the same time, in order to increase the electrical conductivity of transparent contacts of SnO and CdO, these films were doped by adding antimony and fluorine to the initial substance. Photosensitive films are made by thermal evaporation of powdered CdSe on glass substrates previously coated with a transparent conductive layer of SnO2 or CdO at a temperature of 250-400°C (Fig. 1). The second electrode (upper electrode) was In or Al, in some cases a pressure contact was used. heat treatment (MOT) in vacuum, in the air in the presence of CdCl2 or CuCl2 at a certain temperature and time interval.

Technology

The maintenance process was carried out in a specially designed quasi-closed chamber (Fig. 2), the design of which does not allow direct ingress of impurities on the surface of the films, a gaseous environment of sensing substances is formed in it and the maintenance process can be carried out in air or in vacuum. Optimal volume selected

chamber, which provides the necessary partial pressure of vapors of sensing substances at 400-500 ° C. The proposed method of film maintenance provides uniform diffusion of atoms of sensing substances, which is confirmed by the results of experimental studies.

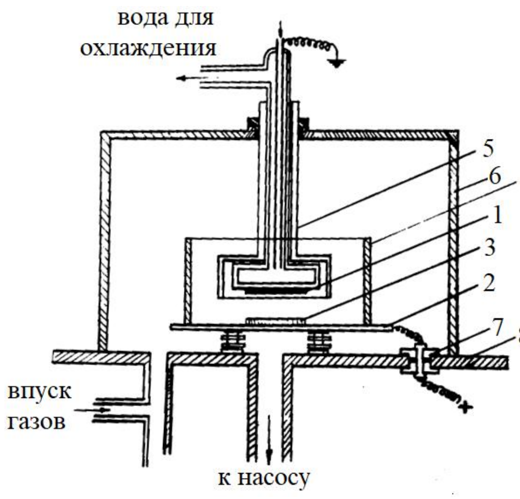
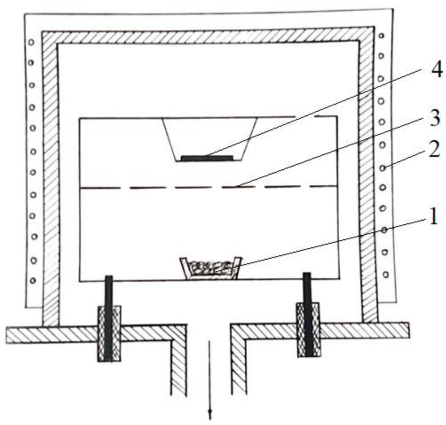


Fig.1. Schematic view of the cathodic sputtering unit. 1 – cathode, 2 – anode, 3 – substrates, 4 – quartz cup, 5 – insulating jacket, 6 – glass cap, 7 – insulator, 8 – metal plate.



Rice. 2. Schematic view of the camera for sensing films in various environments. 1 - crucible with copper or cadmium halides; 2 - stove; 3 - curtains; 4 - holder of freshly prepared films.

The films of cadmium oxide and tin dioxide obtained by us had sufficient mechanical strength and chemical stability. Doping directly in the process of deposition made it possible to obtain films with high transparency and electrical conductivity. During the formation of photosensitive layers, the characteristics of the films are significantly influenced by the amount of impurities introduced, the oxygen content in the spray chamber and the value of the atomization parameters. The amount of Sn in the cadmium cathode for the resistance and transparency of cadmium oxide films at the optimal ratio of gases in the spray chamber is shown in Table 1. It can be seen that with small amounts of impurity the conductivity changes insignificantly, and with an increase in the content of impurity in the cathode, the conductivity of the layers increases. 10-15 batches of CdO were obtained from each cathode specimen with reproducible electrical and optical characteristics. In this range of impurities, the light transmission

Table 1 Dependence of resistance and transparency of SnO2 films on the Sn content in the Cd of the cathode

Sn content in Cd of the cathode, mg	Resistance, Ohm	Transparency, %
0	300	65
0,3	250	70
1,15	170	70
1,28	150	85
2,5	100	80
4,5	90	73

Varied from 65 to 85% depending on the thickness of the films. Films obtained by spraying in air or oxygen were opaque, but when annealed in air, they became transparent. In our experiments, the films were transparent without subsequent annealing. The study of the effect of the composition of the gas mixture in the spray chamber on the characteristics of the films revealed (Table 2) that these characteristics are strongly related to the spray rate.

Table 2 Dependence of Resistance and Transparency of SnO_2 Films on the Oxygen Content in the Spray Chamber

Oxygen content in the spray chamber, %	Resistance, Ohm	Transparency, %
20	80	70
80	95	77
50	110	75
70	150	80
90	300	80

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We have found that with a decrease in the oxygen content in the mixture, the spray rate increases and vice versa. Resistance increases with an increase in the oxygen content in the spray chamber (Table 2).

Discussion of the Results

In order to clarify the occurrence of high PF after maintenance of freshly prepared films in various media, the kinetics of the sensing process was studied (Fig. 3). In the initial time of

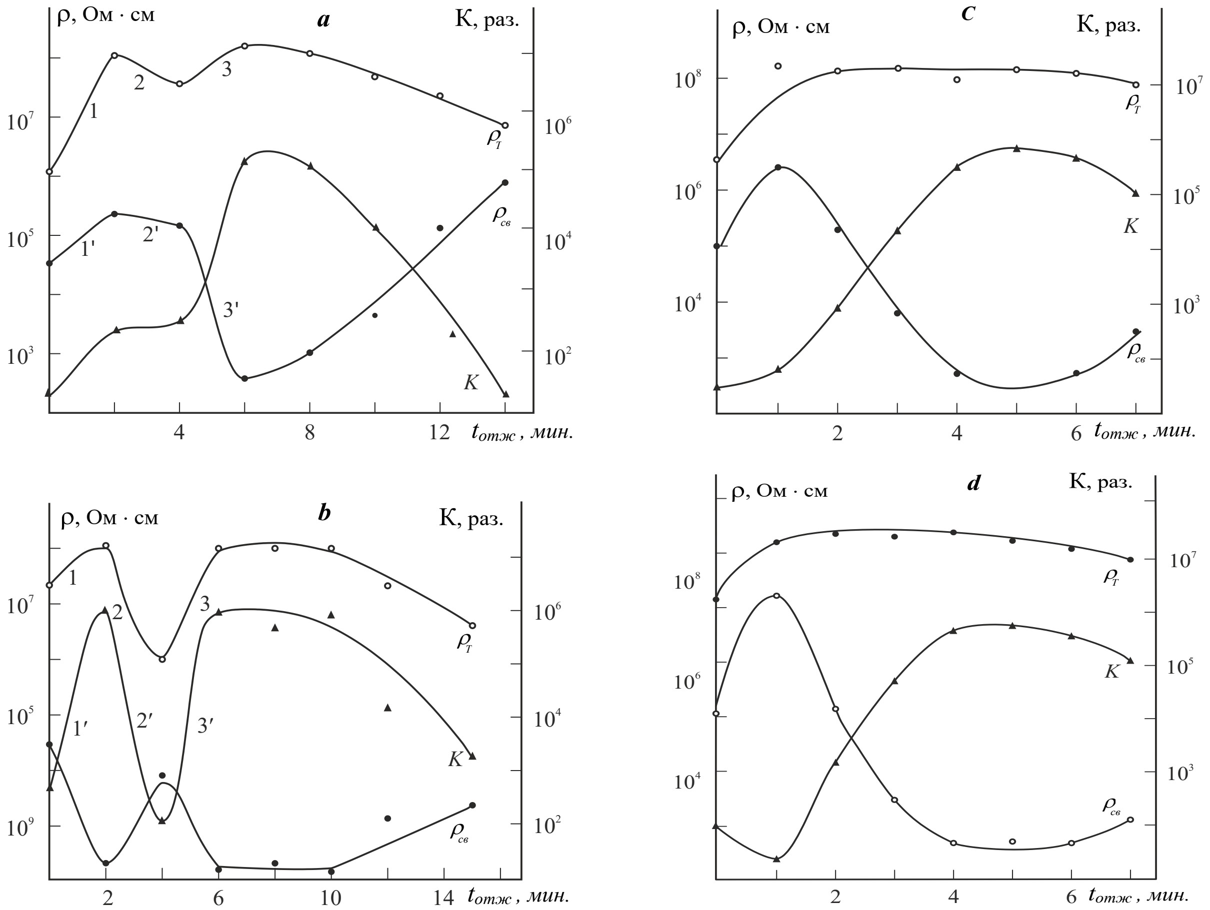

Fig.3. Dependences $\rho_{of\ T}$, ρ_{sv} and K on the time of maintenance in air for CdSe films in the presence of CdCl2 (a, b), CuCl2 (c, d) obtained at Tp = 250 °C (a, c) and Tp = 400 °C (b, d).

maintenance in air in the presence of CdCl2 films obtained at T = 250°C, an increase in

ρ ρ In this case, the oxidepenetrates mainly along the cleavage planes of microcrystallites and, interacting with their faces, changes the charge state, which leads to an increase in the bending of energy zones, i.e. the size of potential barriers for the main charge carriers. The results of the study of the film substructure show that in this area of technical inspection there is an increase in the size of coherent X-ray scattering, a decrease in the minimum dislocation density, and a slight increase in the number of hexagonal modifications, i.e. began to rewritethe

films. This is accompanied by the appearance of excessive vacancies, which leads to an increase in the concentration of donor and acceptor levels. An increase in PF is observed.
A further increase in the MOT time leads to slightchanges in photosensitivity due to the introduction of dissociated chlorine vacancy atoms and the replacement of selenium vacancy (VSe) and the formation of small donor levels. Then the interstitial concentration of chlorine increases (TOJ = 4 - 6 min.). Since there is a dynamic equilibrium between the vacancy of cadmium (VCd) and its interstitial atoms, the increase in the concentration of chlorine, leading to the reaction of chlorine with interstitial cadmium, disturbs this equilibrium. The formed CdCl2 leaves the crystallites, and the concentration of V_{Cd} increases. This leads to a compensation of conductivity and an increase in ρt. As a result of an increase in the concentration of sensitivity centers, ρcv decreases. An increase in the PF is observed. In the interval of maintenance time of 6-10 minutes, the PF changes insignificantly and its maximum is observed. And then, with an increase in the maintenance time, a decrease in ρt and an increase in ρst are observed. As follows from structural studies, an increase in the perfection of the crystal structure of films, a decrease in the concentration of fast and slow recombination.

Findings:

Methods have been developed for obtaining transparent conductive contacts from SnO_2 and CdO with transparency 70-80% and an electrical resistance of 50-60 Ω on a glass substrate by cathodic sputtering for photosensitive film structures operating in longitudinal mode;
Technologies for obtaining photosensitive films CdSe:Cd,Cu,Cl have been developed, including the application of a photosensitive layer of CdSe to a substrate in a vacuum and its sensing by means of maintenance in a quasi-closed chamber in a vacuum, in the air in the presence of $CdCl_2$ or CuCl2 vapors, providing uniform diffusion of impurities.
It has been experimentally established that photosensitive films with stable and reproducible-electrophysical characteristics are obtained at annealing temperatures: in air in the presence of $CdCl_2$ -470°C; CuCl 2-300°C; in vacuum, 480°C.

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