Thermal vacuum method for producing photoconductive CdSe films with transparent SnO_2 contacts

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ABSTRACT

The paper proposes a method for obtaining contacts with 70-80% transparency (at 700-720 nm) and a resistance of 90-110 Ohms using cathodic sputtering from a mixture of SnO_2 and CdO onto a glass substrate. This is done by preliminary thermal evaporation of an Sn layer onto the Cd cathode surface in high vacuum. The method for manufacturing a photosensitive CdSe film is also developed, which involves thermovacuum deposition of CdSe onto a substrate with a transparent SnO_2 layer, followed by thermal treatment of the freshly prepared film in a quasi-sealed chamber in the air in the presence of $CdCl_2$ or $CuCl_2$ vapors, ensuring uniform diffusion of photosensitive substances.

Keywords: Thin films, photodetectors, longitudinal photoconductivity, transparent contact, cadmium selenide, tin dioxide, cathodic sputtering, thermovacuum deposition.

Introduction.

Semiconductor binary compounds A_2B_6 and solid solutions based on them are widely used in the manufacture of photodetectors for the visible spectrum, thin-film emitters, acoustic devices for various purposes, and as the active medium for producing photoresistors, photodiodes, and solar cells [1-5]. The study of longitudinal photoconductivity in A_2B_6 semiconductor compounds is also significant due to the increasing use of films of these compounds in the development of longitudinal photoresistors, which offer advantages over transverse ones, such as higher utilization of the receiving surface, higher sensitivity to current, and more. Among A_2B_6 compounds, cadmium selenide is the most sensitive in the visible and near-infrared spectral range. The achievements made in recent years in the technology of producing polycrystalline CdSe films operating in the longitudinal photoconductivity mode have led to the development of several photoelectronic devices for micro- and optoelectronics, acousto-electronics, automation, and nonlinear optics.

A widely used method for producing CdSe films is vacuum deposition at temperatures of 200-400°C. Freshly prepared films generally have low photoconductivity. An effective way to vary the photoelectric properties of cadmium selenide films is their thermal treatment (HT) in a vacuum, in air, under a flux containing various chlorides, etc. During the HT process, changes in electrophysical properties occur, along with changes in phase composition, crystal lattice parameters, dominant crystallite orientation, block sizes, and microdeformations of the lattice. However, the issues of technology for obtaining and the effect of structural defects on the photoelectric properties of CdSe films in the longitudinal photoconductivity mode have not been thoroughly studied, which is the focus of the present work.

Technology for the production of transparent conductive layers from SnO_2.

When implementing the longitudinal photoconductivity mode, one of the contacts must be optically transparent to the spectral range of the photosensitive film being studied. The range of materials combining high optical transparency in the visible spectrum, where compounds from the A_2B_6 group exhibit maximum photoconductivity, is limited. Oxide films of SnO_2 are the most commonly used [6]. Transparent conductive films, particularly SnO_2, are produced by thermal evaporation, pyrolytic decomposition, cathodic sputtering, and other methods [see, for example, 7,8].

In the work [7], SnO_2 layers were obtained by thermally evaporating metallic tin in a vacuum followed by thermal oxidation. The formation of the oxide layer is described by the following main reactions occurring simultaneously:

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

This method produces loose, high-resistance layers with resistances ranging from 10^5 to 10^8 ohms.

Many authors ([6,7]) use the method of tin chloride pyrolysis to produce SnO_2 layers. The reaction for the formation of the layer can be represented by the following main equations:

$$SnCl_2+H_2O\rightarrow SnO+2HCl\uparrow, \quad \begin{matrix} 2SnO+2O_2\rightarrow 2SnO_2 \\ 2SnO\rightarrow Sn+SnO_2 \end{matrix} \quad > 380^oC$$

When using this as the starting material, the formation reaction can be expressed as:

$$SnCl_4+2H_2O\rightarrow SnO+2HCl\uparrow,$$
$$SnO_2+regenerator\rightarrow SnO,\ 2SnO\rightarrow Sn+SnO_2$$

The process of layer formation lasts several minutes. Using the pyrolysis method of tin chloride, SnO_2 layers with electrical resistance from several ohms to hundreds of thousands of ohms can be obtained.

From the formation reactions, it can be seen that the film forms from the dioxide, with conducting impurities of SnO and Sn present. The transparency and conductivity of the layer depend on the content of these impurities in the film, which cause the non-stoichiometry of the film composition.

Another progressive method for producing SnO_2 layers is reactive cathodic sputtering of metallic tin. Unlike other methods, cathodic sputtering allows for uniform deposition of films with controlled thickness due to the use of a large surface-area source, ensures high stoichiometry of the deposited layers, and produces high-purity films at low temperatures. This process has low inertia and is easily controlled [9]. Sputtering is carried out in an atmosphere of oxygen mixed with an inert gas. Argon, nitrogen, and other inert gases are commonly used. The rate of growth of the resulting films is significantly influenced by the voltage, discharge current, gas composition and pressure, as well as the distance between the electrodes. Depending on these parameters, the method of introducing and the amount of impurities, the electrical and optical properties of the resulting films can vary widely. Authors of work [6] found that films deposited at substrate temperatures of 390-430°C have densely packed grains, a smooth surface, and the sizes of micro-inhomogeneities in the plane of the substrate range from 540-1000 Å. Further increase in substrate temperature (450°C) leads to the formation of needle-like microcrystals, and the size of micro-inhomogeneities reaches 1000-2000 Å. After annealing in air, electrical conductivity increases due to the dominant process of tin oxide dissociation, smoothing of the micro-relief of the surface, and improved contact between the grains. As the film thickness increases, electrical conductivity and the integral transmittance coefficient decrease, which is particularly explained by the enlargement of the microcrystals.

Films produced by pyrolytic decomposition or cathodic sputtering are high-resistance. To increase the electrical conductivity and transparency of SnO_2 films, they are often doped by adding antimony, fluorine, hydrochloric phenylhydrazide, zinc, bismuth, and other elements to the starting material [9]. Optical and electrical properties of SnO_2 films have been studied to modify their electrical properties by choosing antimony as an impurity, since the ionic radius of Sn4+ (0.71 Å)

is close to the ionic radius of Sb (0.62 Å), and antimony has one excess electron compared to tin. Naturally, antimony ions, replacing some Sn atoms in the SnO_2 structure, form new donor levels in the forbidden zone, leading to increased electrical conductivity. It was found that when 75 ml of $SnCl_4$ was doped with 96 g of $SbCl_2$, the transmittance and specific resistance of the SnO_2 film were 80% and 50 ohm·cm, respectively.

We have developed an effective method for doping SnO_2 films with cadmium during their preparation on a glass substrate by cathodic sputtering, based on the results from works [10,11]. In the setup (Fig. 1) for reactive cathodic sputtering, the cathode was a tin plate, and a thin layer of cadmium with a thickness of 0.02-0.03 μm was applied to its surface before sputtering in high vacuum. The cathode holder design ensured the circulation of a liquid coolant inside the cathode to maintain its temperature within certain limits. The anode consisted of an aluminum block with a heating plate inserted, on which 2-4 substrates were placed simultaneously. The substrates were standard glass plates of size 3.0x1.0x0.3 cm^3, which were pre-treated with nitric acid, then boiled in distilled water for 15-20 minutes, and dried and wiped with alcohol. To obtain a tin oxide film, a thin cadmium layer with a thickness of 0.08 μm was also deposited on a tin plate by thermal evaporation in a vacuum of ~10^{-4} mm Hg, and the plate was placed as a cathode in the sputtering setup. The chamber was filled with a mixture of inert gas in the ratio of 15-20% Ar and 80-85% O_2. Sputtering was carried out with a current density of 1.45-1.5 mA/cm^2 (E = 2 kV/cm) in a vacuum of 10^{-2} mm Hg at a rate of 90-100 Å/min to form SnO_2 films with cadmium impurities on the glass substrate. The transparency and resistance of the films were 70-80% (at 700-720 nm) and 90-110 ohms, respectively. The adhesion properties of the films produced by this method are improved, ensuring their chemical stability and increasing the reliability of devices based on semiconductor films.

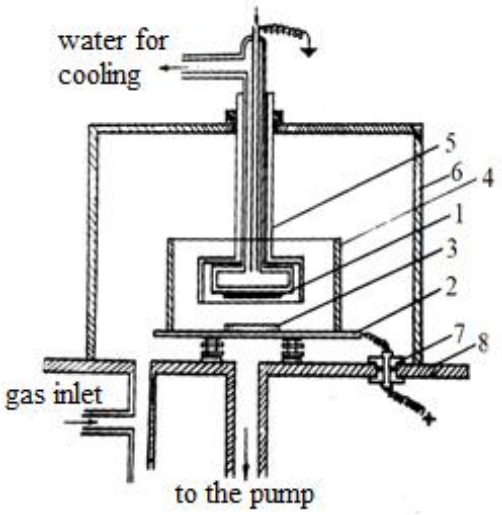

Fig. 1. Schematic diagram of the setup for obtaining a trnsparent electrode by the method of cathodic sputtering. 1 – cathode; 2 – anode; 3 – substrates; 4 – quartz glass; 5 –

Methodology for Obtaining Cadmium Selenide Films.

Cadmium selenide films were produced by thermal evaporation of CdSe onto glass substrates with an SnO_2 layer in a vacuum setup VUP-5M, the main chamber of which is schematically shown in Fig. 2. The starting material used was powdered cadmium selenide of the "for semiconductors" grade. Evaporation was performed from an alumina or beryllia crucible in vacuum at a residual pressure of 10^{-5} mm Hg. Before establishing the stationary evaporation mode, the crucible was closed with a shutter before each deposition. This allowed for maintaining a constant composition of the vapor flux and more accurately controlling the deposition time.

The substrates used were glass, previously coated with a transparent conductive layer of tin dioxide (SnO_2) with a thickness of 0.1-0.3 μm. Before deposition, the substrates were cleaned by treatment in boiling 0.5% nitric acid solution, then degreased in acetone, and boiled in distilled water. Additionally, just before deposition, the substrates were heated in vacuum at 400°C for 30 minutes. The substrates were heated using a furnace whose design allowed the substrate temperature to be varied up to 600°C (Fig. 2).

The temperature of the substrate and the evaporator during deposition and condensation was controlled by chromel-alumel thermocouples mounted directly on them. The thickness of the resulting films was determined using an interference microscope MII-1 and ranged from 5 to 20 μm. To avoid

direct exposure of the substrate to sublimated atoms, the surface of the crucible was covered with a quartz plate.

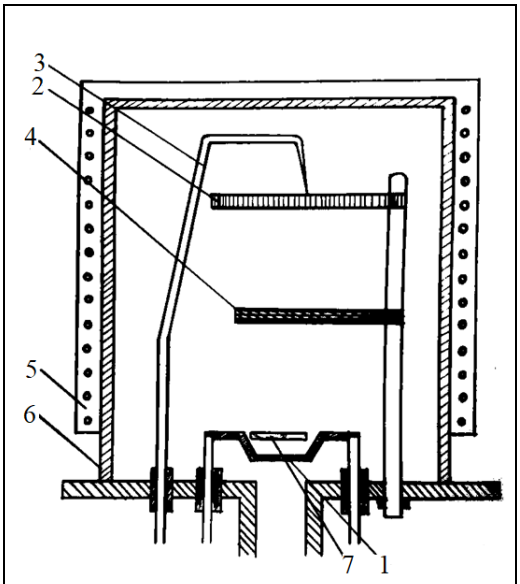

Fig. 2. Schematic view of the vacuum chamber for obtaining CdSe films. 1 - Evaporator; 2 - Substrate holder; 3 - Thermocouple; 4 - Shutter; 5 - Furnace; 6 - Quartz bell.

For comparison of the electrophysical properties of photosensitive films in longitudinal and transverse configurations, CdSe layers were also deposited on "clean" substrates. In the longitudinal configuration, the second electrode was made of layers of In, Al, or a pressure contact.

It is known that the electrophysical properties of CdSe films significantly depend on technological parameters such as evaporation rate and substrate temperature. Cadmium selenide is a compound that dissociates when heated. Depending on the dissociation and sublimation energy, CdSe decomposes into atoms and molecules. A change in the evaporation rate leads to a change in the density of the flow of dissociated Cd and Se atoms from the crucible, which, in turn, leads to a change in the condensation rate of these atoms onto the substrate. On the other hand, it is known that at sufficiently low temperatures the coefficient of condensation $\alpha_k=R_k/R_I=1$ and $R_k=R_I$, where R_k -is the density of the condensed flow, R_I - is the density of the sublimated flow. With an increase in the temperature of the substrate T_s, the amount of the flow of desorbed atoms $R_g=R_I-R_k$ from the surface of the substrate and $\alpha_k<1$ increases noticeably, which leads to a decrease in the rate of condensation. Based on this, it can be concluded that the deposition rate of the films can be controlled by the substrate temperature while maintaining a constant evaporation temperature and the initial mass of CdSe. Therefore, in this work, greater attention was given to studying the effect of the substrate temperature on the electrophysical properties of the films obtained. It was found that the best films with good electrophysical properties were formed at deposition temperatures in the range of 200-400°C.

Freshly prepared cadmium selenide films have low photosensitivity. Therefore, to increase the photosensitivity, the films were subjected to thermal treatment (HT) in air, vacuum, and in a gas environment of cadmium chloride or copper chloride. For the HT of freshly prepared films, a furnace consisting of two parts was used (Fig. 3). In crucible 1, which is located at the bottom of the chamber, cadmium or copper halides were placed. The films were placed in the upper part of the chamber. The haloid gases formed during heating entered the upper part of the chamber through small-diameter holes 2. The design of the furnace prevented direct contact of impurities with the film surface 4. An optimal chamber volume was selected to ensure the necessary partial pressure of vapor of sensitizing substances at 400-500°C. The chamber was connected to a vacuum system, which allowed for a pressure of 10^{-5} mm Hg to be created inside. In this furnace, the HT of freshly prepared films was carried out in vacuum, air, and in the gas environment of $CdCl_2$ or $CuCl_2$.

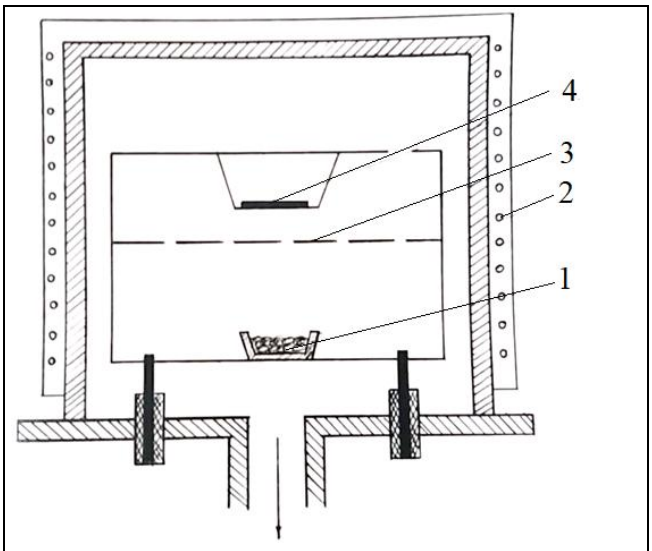

Fig. 3. Schematic view of the chamber for sensitizing films in various media. 1 - Crucible with cadmium or copper halides; 2 - Furnace; 3 - Shutters; 4 - Holder for freshly prepared

ANALYSIS OF THE OBTAINED RESULTS.

The results of the experiments showed that the composition and properties of the formed films are strongly influenced by the composition of the preliminary treatment of the starting material and the evaporation conditions. Changing the substrate temperature significantly affects the resistance of the films (Fig. 4).

The effectiveness of the substrate temperature's influence on the resistance depends on the preliminary treatment of the starting material before evaporation. It is known that CdSe dissociates when heated:

$$CdSe_{solid} \leftrightarrow Cd_{gas} + \frac{1}{2} Se_2$$

Depending on the dissociation and sublimation energy, CdSe decomposes into atoms and molecules. During the initial condensation period, due to the partial reflection of Se in the film, an excess of cadmium is formed, leading to low resistance. As the substrate temperature increases, the reflection of cadmium from the surface of the substrate begins, and the composition becomes more stoichiometric, causing the resistance of the films to increase with the substrate temperature.

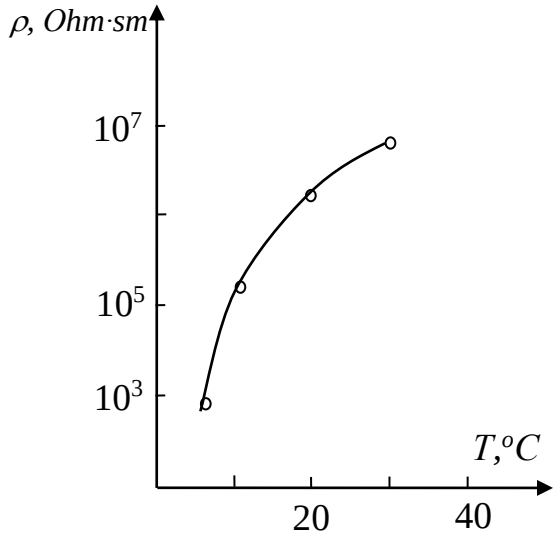

Fig. 4. Dependence of the specific resistance of the CdSe film on the substrate temperature

According to X-ray diffraction and electron microscope analysis, the structure of the freshly prepared CdSe films is polycrystalline, with reflections characteristic of the cubic and hexagonal modifications of CdSe, with prominent (311) lines.

Measurements showed that these films exhibit high electrical conductivity, especially the films prepared at low substrate temperatures. The X-ray diffraction patterns revealed reflections corresponding to excess cadmium. Measurements of the temperature dependence of the films' conductivity showed that the activation energy is 0.6 eV, which is typical for donors in CdSe. Thus, freshly prepared films exhibit high electrical conductivity due to the excess cadmium.

Conclusion.

A transparent contact made from a mixture of SnO_2 and CdO was obtained on a glass substrate by cathodic sputtering, with a transparency of 70-80% (at 700-720 nm) and a resistance of 90-110 Ohms. This was achieved by preliminary thermal evaporation of an Sn layer onto the Cd cathode surface in high vacuum. A method for manufacturing photosensitive CdSe films was developed, involving thermovacuum deposition of CdSe onto a substrate with a transparent SnO_2 layer, followed by thermal treatment of the freshly prepared film in a quasi-sealed chamber in the air in the presence of $CdCl_2$ or $CuCl_2$ vapors, ensuring uniform diffusion of photosensitive substances.

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