CRYSTALLINE STRUCTURE AND OPTICAL PROPERTIES OF CDS FILMS PREPARED BY MAGNETRON SPUTTERING WITH DIRECT CURRENT

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Abstract

In order to create a cost-effective, suitable for large-scale application technology on forming a layer of a wide-band "window" for the thin-film photovoltaic converters based on cadmium sulfide and telluride we have carried out experimental studies of the dependence of optical properties and crystalline structure on temperature of the cadmium sulfide films deposition obtained by magnetron sputtering with direct current. By the two-channel optical spectroscopy method it has revealed that the cadmium sulfide film deposition at a temperature of 160 °C allows creating layers with band gap of 1.41 eV that is close to the value typical for single crystals, and the density of the photon flux passing through the cadmium sulfide layer in the cadmium telluride photosensitivity spectral range at a level 37.0 W nm cm2.

These two parameters determine the amount of optical loss of film photovoltaic converters based on cadmium telluride sulfide with the back configuration in the wide-band "window" layer.

Using X-ray diffraction methods it was demonstrated that by increasing the deposition temperature from 100 °C to 160 °C the growth of the size of coherent scattering regions, and decrease in the macrodeformation level have a decisive impact on the reduction of the optical losses in the CdS films formed on glass substrates. According to the elemental analysis results with further increase of the deposition temperature to 230 °C the experimentally observed increase in optical losses of cadmium sulphide films occurs as a result of thermally activated depletion of these layers by a volatile sulphur component.

Keywords: Cadmium sulfide films, method of magnetron sputtering with direct current, optical loss, band gap, crystalline structure.
1. Introduction

In modern designs of film photovoltaic converters (PVC) based on back configuration cadmium telluride the wide-band "window" effect is used to reduce the surface recombination rate of nonequilibrium charge carriers generated by light [1]. This effect consists in removal of the areas with active generation of nonequilibrium charge carriers from the defect illuminated surface by using in the PVC film designs of the wideband semiconductor materials having high transmittance in the spectral region corresponding to the region of spectral photosensitivity of the base layer. Numerous experimental studies (see. e.g., [2, 3]) showed that for film photovoltaic converters with a base layer of cadmium telluride as the wide-band "window", the best solution is the use of thin films cadmium sulfide. Cadmium sulfide for film photovoltaic converters is traditionally produced by the following methods: thermal vacuum evaporation, deposition in a closed volume, chemical vapor deposition and high-frequency magnetron sputtering [4, 5]. CdS films obtained by these methods have a stable wurtzite crystalline structure, a high transmittance in the spectral range corresponding to the photosensitivity range of cadmium telluride, exhibit good adhesion to the transparent front electrode layer deposited on the glass substrate. The most effective designs of film photovoltaic converters with the base layer of cadmium telluride use CdS films obtained by chemical deposition with a thickness of less than 100 nm [6]. However, the chemical vapor deposition method is difficult to adapt to the mass production conditions, because it is characterized by low rates of growth of cadmium sulfide film. Upon that, it is necessary to address the issues of regeneration of liquid chemical waste. More technologically advanced in terms of mass production is the method of thermal vacuum evaporation. However, studies conducted (for example, see [7]) showed that the thickness of the cadmium sulfide films obtained by this method for their use in photovoltaic converters based on cadmium telluride should be at least 0.3 microns. Otherwise, due to the through porosity of the cadmium sulfide films obtained by this method what arises due to the geometric effect of shading the surface by fastest growing grains there occurs bypassing of a separation barrier of the device structure due to the electrical contact of the base layer of cadmium telluride to the front electrode. The cadmium sulfide films prepared by the magnetron sputtering method do not have this deficiency. However, large scale industrial application of this method is limited by the high cost of a high-frequency power source. At the same time, cost-effective and well mastered by the domestic electronic industry method of non-reactive magnetron sputtering with direct current is almost not used for CdS films production. Thus, the experimental studies of the influence of nonreactive magnetron sputtering parameters with direct current on the crystalline structure and optical properties of CdS films are relevant for the creation of industrial vacuum
technologies intended for producing wideband "windows" for film photovoltaic converters with a base layer of cadmium telluride having back configuration.

2. Experimental technique

To make cadmium sulfide films by non-reactive magnetron sputtering with direct current [8], there was designed and manufactured a magnetron adapted to the design of a standard industrial vacuum plant UVN 71-P3 (Figure 1). Installation of the magnetron was carried out through the viewing window of the vacuum plant (Figure 1, c).

![Diagram and photos of the magnetron system](image)

The magnetron design has enabled the efficient use of the target material. This was due to the fact that upon 100 mm diameter magnetron, the diameter of the erosion zone was 65 mm, and its width was 10-12 mm. Such erosion zone dimensions allowed deposition of the film with size of 70 mm by 70 mm with a thickness uniformity of 5%.

Therefore, the magnetron system applied for making films can be used in the conditions of an industrial production. A special tool made it possible to move the substrate along with the heating section and the heat-insulating screen in a horizontal plane to a position in which a target pollution excluded during preheating. The source of the sputtering material was a target 1 which is a disc having 10 cm in diameter pressed from 99.99% CdS powder. The target was located on the surface of the water-cooled magnetron. At the bottom of the anode of the magnetron there was an entry for the tube through which argon and oxygen gas mixture has been fed into the sputtering system. The developed design of radiation heating the substrate in the capacity of which 2 mm thick glass plates K8 are used, has allowed uniform heating the substrate area to the set temperature in the range of 100-220 °C and maintain the temperature to
within ± 2 °C by means of an automatic control system. The total pressure of the sputtering gas required for stable operation of the magnetron was 2 Pa. Therefore, between the working chamber and the pump there was installed a restricting orifice required for stable operation of the diffusion vacuum pump at this low pressure. The distance from the substrate to the target that was 35 mm has been defined as the minimum at which the inhomogeneity of the produced film by thickness did not exceed 5%, taking into account the geometric factor. The crystalline structure and phase composition of the films were examined with use of the X-ray diffractometer DRON-4M in monochromatic Co-Kα radiation. Phase identification in the samples was carried out by comparing the set of interplane distances calculated from Bragg equation [9] with the existing sets of interplane distances for tin oxides from ASTM reference cards. Initial processing of the diffraction peaks was carried out using a developed computer program. This treatment allowed us to determine the position of the diffraction peak (2θ), the interplane distance (d) and integrated intensity (I). The spectral dependence of the transmission and reflection coefficients of cadmium sulphide films was studied by dual-channel optical spectroscopy using a spectrophotometer SF-2000 equipped with the attachment SFD-2000 to measure the mirror and diffuse reflections. The optical band gap \( E_g \) in CdS layers was determined as described in [9] by means of extrapolation to the energy axis of a linear section of the dependence \[-ln (T) \cdot h\nu \]^2 on \( h\nu \).

3. Results and their discussion

3.1 Study of the admium sulphide films optical properties

Cadmium sulphide films were prepared by magnetron sputtering with direct current at a working gas pressure of 0.9 - 1 Pa, a discharge voltage of 550 - 600 V, and a current density of 0.44 - 0.53 mA / cm^2. Upon that, deposition temperature was varied from 100 °C to 230 °C. Such parameter ranges of technological modes may be considered suitable for reproduction in an industrial environment. Time of film deposition was 5 minutes.

Study of optical properties of cadmium sulphide films was carried out by measurements of the spectral dependence of the transmission and reflection coefficients of CdS films within the spectral range 400-1100 nm (Figure 2). Analysis of transmission spectra shows that all samples except for the sample obtained at a deposition temperature 100 °C demonstrate strong absorption within the wavelength range 400 - 500 nm and a sharp absorption edge in the range 500 - 550 nm. Upon that, in the red and infrared regions of the spectrum there is a high transparency at the level of 80%. Analytical processing of transmission and reflection spectra allowed us to determine the optical parameters of the films under study obtained at different deposition temperatures.
Figure 2 - Spectral dependences of transmission coefficients for cadmium sulfide films obtained at different deposition temperatures.

Figure 3 shows the results of determining the band gap \( (E_g, \text{eV}) \) and the theoretical luminous power values \( (W, \text{W nm cm}^{-2}) \) for the light flux that can pass through the investigated cadmium sulfide film under illumination equal to AM 1.5, within the spectral range of photosensitivity of photovoltaic converters based on cadmium sulfide and telluride that is equal to 550-900 nm according to published data [8]. These two parameters determine the value of optical loss in the cadmium sulfide layer when it is used as the wide-band "window" in the film photoelectric converters with the base layer of cadmium telluride of back configuration. Optical studies have shown that with increasing the deposition temperature to 160 °C there is an increase of luminous power passed through the cadmium sulfide film from 32.7 W nm cm\(^{-2}\) to 37 W nm cm\(^{-2}\). Further growth of the deposition temperature to 230 °C leads to a decrease in transmitted luminous power to 33.5 W nm cm\(^{-2}\). Analysis of Figure 3 shows that increasing the deposition temperature from 100 °C to 160 °C causes an increase in band gap from 2.38 eV to 2.41 eV.

Figure 3 - Optical parameters of CdS films prepared by magnetron sputtering.

Further growth of the deposition temperature from 160 °C to 230 °C leads to a decrease in the width of the band gap from 2.41 eV to 2.39 eV. According to the literature [4] band gap is 2.42 - 2.45 eV for the single-crystal cadmium sulphide films. Lower values for the band gap of polycrystalline cadmium sulfide films, in comparison with single
crystals, are due to the fact that the grain boundaries absorb light as metal layers what leads to a decrease in the value of the band gap determined by optical methods.

In addition to the developed grain boundary surface, decrease in the optical band gap may be caused by depletion in cadmium sulphide films of sulfur volatile component.

Thus, the design of high-performance photovoltaic converters based on cadmium sulfide and telluride should use the films obtained at the deposition temperature of 160 °C because this provides maximum photon flux density received by the base layer of cadmium telluride that allows increasing the efficiency due to growth of short circuit current density.

3.2 Research of crystalline structure and elemental composition of cadmium sulphide films.

To identify the physical mechanisms that determine the dependence of the band gap of cadmium sulfide films obtained by magnetron sputtering with direct current, researches of a crystalline structure of films have been carried out with use of X-ray diffraction method (Figure 4). The experimental X-ray diffractograms demonstrate only one peak at an angle $2\theta = 30,62^\circ$ what corresponds to the reflection (111) of cubic modification or reflection (002) of the hexagonal CdS phase that are characterized theoretically by the maximum intensity. Due to the small thickness of the sample other diffraction peaks were not identified that did not allow us to determine the phase composition of CdS samples by X-ray diffraction method. Nevertheless, taking into account the fact that the stable modification of CdS is hexagonal, further processing of X-ray diffractograms under study was conducted for CdS hexagonal phase. The results of analytical processing of structural research data are presented in table 1

![Figure 4 - X-ray diffractograms of cadmium sulfide films obtained by magnetron sputtering with direct current at different deposition temperatures.](image-url)
Table 1 - Results of the analytical processing of structural research data for CdS films prepared by magnetron sputtering with direct current.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>T_{deposit}, °C</th>
<th>Peak position, degree.</th>
<th>Interplanar distance ((d_{002}), \text{ Å})</th>
<th>Half-width of the diffraction peak ((\Delta \Theta), \text{ degree.})</th>
<th>L, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>30.58</td>
<td>3.391</td>
<td>0.38</td>
<td>25.2</td>
</tr>
<tr>
<td>2</td>
<td>130</td>
<td>30.62</td>
<td>3.388</td>
<td>0.33</td>
<td>29.0</td>
</tr>
<tr>
<td>3</td>
<td>160</td>
<td>30.59</td>
<td>3.391</td>
<td>0.33</td>
<td>29.0</td>
</tr>
<tr>
<td>6</td>
<td>190</td>
<td>30.64</td>
<td>3.385</td>
<td>0.34</td>
<td>28.1</td>
</tr>
<tr>
<td>5</td>
<td>230</td>
<td>30.70</td>
<td>3.379</td>
<td>0.30</td>
<td>31.9</td>
</tr>
</tbody>
</table>

With increasing deposition temperature from 100 °C to 230 °C, a decrease in the interplane distance (002) from \(d_{002} = 3,391 \text{ Å}\) to \(d_{002} = 3,379 \text{ Å}\) that corresponds to a decrease of the parameter \(c\) of a hexagonal lattice from \(c = 6,782 \text{ Å}\) up to \(c = 6,758 \text{ Å}\). These parameter \(c\) values are higher than the table value which is characteristic to single crystals \((c = 6,7198 \text{ Å})\). This indicates the presence of compressive macrostresses the value of which decreases with increasing temperature up to 230 °C. With increasing deposition temperature from 100 °C to 230 °C, a decrease in physical broadening of the diffraction peak from \(\Delta \Theta = 0.38\) to about \(\Delta \Theta = 0.30\) is observed. The estimation of the presented widths of the diffraction peak shows that with increasing deposition temperature the growth of coherent scattering regions from 25.2 nm to 31.9 nm is observed.

Thus, with increasing deposition temperature from 100 °C to 230 °C, a logical increase in the quality of the crystalline structure of cadmium sulfide films is observed: a decrease in the level of macroscopic stresses and increase in the size of coherent scattering regions is observed what reduces the light absorption at the developed grain boundary surface. The reduction of microstrain level and increase in the size of coherent scattering regions cause the growth of the optical band gap.

The crystalline structure researches were complemented by researches of the elemental composition of the films obtained, which were held with use of "Elvatech" spectrometer manufactured by ElvaX company. Pulse time made 240-241 per second. Researches have shown (Fig. 5) that with increasing deposition temperature from 100 °C to 230 °C the ratio of the atomic concentration of sulfur \((C_S)\) to the atomic concentration of cadmium \((C_{Cd})\) is decreases from \(C_S/C_{Cd} = 1.06\) to \(C_S/C_{Cd} = 0.95\) that is associated with the depletion of the growing film of highly volatile component which is sulfur.
Figure 5 - The ratio of the atomic concentrations of sulfur and cadmium in cadmium sulfide films obtained by magnetron sputtering with direct current at various deposition temperatures.

Thus, with increasing deposition temperature a decrease in the degree of the stoichiometry of the films that is due to the increase in the vacancy concentration causing increased light absorption and decrease of the effective optical band gap as a result of the appearance inside the band gap of energy levels capable of participating in the light activated transition of charge carriers.

4. Conclusions

As to the cadmium sulfide films used in the construction of film photovoltaic converters of back configuration with the base layer of cadmium telluride, optimum temperature for their deposition by non-reactive magnetron sputtering with direct current is 160 °C due to the achievement of the highest band gap -1.41 eV and a maximum density of the photon flux coming through the cadmium sulfide layer within the spectral range of the cadmium telluride photosensitivity. Extremum in the dependence of the optical properties of the investigated cadmium sulfide films on the deposition temperature is due to the presence of two competing physical mechanisms. The deposition temperature rise up to 160 °C leads to a reducing of the optical losses in the cadmium sulfide films as a result of increasing in the size of coherent scattering regions and reducing the macrodeformation level. With further increase of the deposition temperature to 230 °C the determining factor leading to the growth of optical losses in the cadmium sulfide films is their depletion of volatile sulphur component.

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