Physical and Technological Foundations of the «Chloride» Treatment of Cadmium Telluride Layers for Thin-film Photoelectric Converters

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The process of deposition of cadmium chloride films during the «chloride» treatment of cadmium telluride base layers for thin-film photoelectric converters (PEC) was studied. It is established that to ensure the reproducibility of the thickness and phase composition of cadmium chloride films, it is necessary to take into account the high hygroscopicity of this material. It is shown that the optimal growth rate of cadmium chloride films is 0.1 μm per minute. At high growth rates, cadmium chloride particulates are deposited on the surface of the CdTe layer base, which causes shunting of the PEC during the «chloride» treatment. It is determined that after the «chloride» treatment of CdTe layers, a coarse-grained structure is observed, which is predominantly oriented in the thermodynamic equilibrium direction [422]. In this case, the average grain size increases to 5 μm. It is shown that when performing a «chloride» treatment, the optimum purity of cadmium chloride layers is 98 %, which is due to the doping of CdTe with copper atoms. The disadvantage of copper with the use of more pure cadmium chloride reduces the efficiency of the PEC due to the increase in the series resistivity and the decrease in the photocurrent density. It has been experimentally determined that the optimum thickness of cadmium chloride during the «chloride» treatment and the efficiency of the PEC obtained at the same time depends on the substrate used. Thus, for the ITO/CdS/CdTe/Cu/Au PEC, the optimum thickness of cadmium chloride is 0.40 μm, the efficiency is 9.6 %, and for the NaCl/ITO/CdS/CdTe/Cu/Au PEC – 0.10 μm and 6.4 %, respectively.

Keywords: Photoelectric converter, Cadmium telluride films, Cadmium chloride, X-ray diffractometry, Light current-voltage characteristics, Output parameters, Light diode characteristics.

1. INTRODUCTION

Polycrystalline cadmium telluride films have remained an ideal semiconductor material for economical and efficient photoelectric converters (PECs) for fifty years. This is due to the optimal for photoelectric conversion in terrestrial conditions, the width of the band gap (1.46 eV) and a high optical absorption coefficient [1]. This makes it possible to use as layers of an absorber layer several micrometers thick. On the basis of cadmium telluride base layers, obtained by sublimation in a closed volume, steam transport, thermal vacuum evaporation, electrodeposition and magnetron sputtering, form effective film PEC [2]. The foreign companies of the USA (First Solar, Prime Start Solar, Abound Solar) and Germany (Calyxo, Roth & Rau) launched the industrial production of photovoltaic modules based on cadmium telluride films. The competitiveness of film PEC based on cadmium telluride in comparison with widespread PEC based on crystalline silicon is due to the fact that they have achieved a "network" parity, in which the cost of electricity produced by them is comparable to the cost of electrical energy produced by traditional sources [3].

At the present time, flexible PEC is also being developed on the basis of base layers of cadmium telluride [4]. Such instrument structures have record values of electrical power per unit weight, which is very important for space and military applications of PEC. The obligatory technological operation of obtaining effective PEC based on cadmium telluride is «chloride» treatment [5]. At present, the effect on the crystal structure and photoelectric properties of cadmium telluride films of the «chloride» treatment carried out by precipitation of cadmium chloride from supersaturated solid solutions is investigated.

At the same time, studies aimed at developing the technology of «chloride» treatment when depositing layers of cadmium chloride with high-tech, adapted to mass production by the method of thermal vacuum deposition, with rare exceptions are not carried out.

Investigations of the influence of «chloride» treatment on the crystalline and energy structure of basic polycrystalline layers of cadmium telluride made it possible to identify the basic physical mechanisms that determine the improvement of their photoelectric properties during heat treatment. However, the effect of the «chloride» treatment on the light diode characteristics of the completed instrument structures of the PEC, which is necessary to optimize their design and technological solutions, has not been practically investigated.

Thus, the development of the physical and technological foundations of the «chloride» treatment of film PECs based on sulfide and cadmium telluride in the course of which the application of layers of cadmium chloride is carried out by the method of thermal evaporation is an actual problem.

2. METHODS OF OBTAINING SAMPLES AND RESEARCH

The formation of CdS/CdTe instrument structures was carried out on a glass substrate with a transparent conductive electrode ITO by thermal vacuum evaporation. In a number of cases, sodium chloride films with 1 μm thick were deposited on the glass by thermal evaporation. The deposition temperature of cadmium sulfide films was 200 °C, the thickness of the layers was 0.4 μm. Then, vacuum annealing was carried out at a temperature of 450 °C for 30 minutes. After this vacuum annealing without violating the vacuum at a substrate temperature of 300 °C, CdTe films with 4 μm

thick were deposited. The resulting device heterosystems underwent a «chloride» treatment. To remove reaction products and form surface layers of cadmium telluride enriched with tellurium, the annealed samples were etched in a 5 % solution of bromine in methanol. To form the upper electrodes of the PEC on the etched surface of cadmium telluride, two-layer electrical contacts of Au-Cu were deposited in thermal evaporation. After the formation of the contacts, the PEC was annealed in air at a temperature of 200 °C for 30 minutes.

To perform the «chloride» treatment before the formation of back contacts on the surface of the base layers of cadmium telluride by thermal vacuum evaporation in a laboratory installation B30.2Sach films $CdCl_2$ were deposited. To evaporate the fine-dispersed $CdCl_2$ batch, a molybdenum foil evaporator was made. In the lid of the evaporator a series of holes with a diameter of 0.5 - 0.8 mm were made. This design of the evaporator makes it possible to obtain a uniform vapor flow of the evaporated material. To control the thickness of the deposited layer of cadmium chloride, a quartz resonator placed in the immediate vicinity of the substrate was used in the deposition process. Measurement of the frequency of the quartz generator was carried out by a direct counting frequency counter Ч4-102.

The evaporation of cadmium chloride was carried out at a temperature of (470-475) °C. After deposition, the samples were annealed in air in a SCHOL type furnace at a temperature of 430 °C for 25 minutes.

The X-ray diffraction patterns of the produced cadmium sulfide and telluride films were measured by θ-2θ scanning using a DRON-4 X-ray diffractometer in steps of 0.01 degrees. Determination of the preferential orientation of the films was carried out by analytical processing of the diffraction maxima, according to the maximum texture coefficient C_i. To compare the samples by the degree of texturization, the parameter G [6] was calculated. Precision determination of the lattice period of the investigated films was carried out using the extrapolation function $(\cos^2\theta/\sin\theta) + (\cos^2\theta/\theta)$ [6].

The output parameters of the PEC are the short-circuit current density (J_c), the open circuit voltage (U_{oc}), the filling factor (FF) of the light-voltage current-voltage characteristic (CVC) and, ultimately, the efficiency (η). According to the equivalent PEC scheme, the quantitative characteristics of photovoltaic processes are the light diode characteristics of the solar cell: the photocurrent density (J_f), the density of the diode saturation current (J_0), the diode ideality coefficient (A), the series resistance (R_s) and the shunting resistance (R_{sh}), calculated on SC unit area.

The relationship between the efficiency of the PEC and the light diode characteristics in an implicit form is described by a theoretical light current-voltage characteristic (CVC) [7]:

$$J_l = -J_f + J_o\{exp[e(U_l - J_lR_s)$$
$$/(AkT)] - 1\} + (U_l - JR_s)/R_{sh}, \qquad (1)$$

where J_l is the current density flowing through the load; e is the electron charge; k is the Boltzmann constant; T is the temperature of the solar cell; U_l – volt-

age drop on the load.

The determination of the output parameters and the light diode current-voltage characteristics of the PEC elements based on cadmium telluride was carried out by their experimental light- current-voltage characteristics The light current-voltage characteristics of the solar cells were measured using a laboratory stand when the instrument structures were irradiated by a simulated solar radiation in terrestrial conditions with a luminous flux of 100 MW/cm².

A study of the efficiency of photoelectric processes in film PEC was carried out at the Institute of Semiconductor Physics, V.E. Lashkarova, Academy of Sciences of Ukraine. To obtain a 2D mapping of the photo-current quantum yield distribution, a special scanning system was used, which includes an original 2D acoustic-optical detector. In the system, it is possible to store and process the resulting 2D image. The size of the scanning area is controlled by a special program. When inhomogeneities analyzing by the method of induced currents, a picture of different intensities is obtained. The intensity increase corresponds to the larger value of the induced current; the black portion corresponds to the portion of the instrument structure where there is no potential barrier and no photocurrent generation.

3. RESULTS AND ITS DISCUSSION

3.1 Optimization of Deposition of Cadmium Chloride Films

For the production of cadmium chloride films, evaporation of the cadmium chloride powder with 2.5 aqueous ($CdCl_2 \cdot 2.5H_2O$) grades «ч» GOST 4330-76 was carried out. A quartz resonator was used to control the thickness of the cadmium chloride layer. In the course of a series of experiments it was established that the proportionality coefficient between the magnitude of the frequency shift of the resonator and the mass of the precipitated substance varied nonmonotonically, showing a tendency to constant growth. At the initial stage of heating the evaporator, a sharp increase in the pressure in the chamber from 10^{-6} up to 10^{-3} mm Hg was observed.

In our opinion, this is due to the high hygroscopicity of the $CdCl_2$ compound. The moisture that was sorbed by the surface of the cadmium chloride powder was intensively desorbed at the initial stage of evaporation of the batch, which led to a deterioration of the vacuum in the chamber. The saturation of the cadmium chloride layer formed on the surface of the resonator with atmospheric moisture and the subsequent uncontrolled desorption of moisture immediately upon precipitation led to an «apparent» change in the sensitivity of the resonator to the determination of the mass, which in turn causes a lack of reproducibility of the thickness of the deposited layer and is a serious problem in the development of industrial technology «chloride» treatment.

To analyze the phase composition of the deposited layer of cadmium chloride with X-ray diffractometry, the crystal structure of both the deposited films and the remainder of the sample was investigated after the sample was sprayed.

The obtained experimental data were compared with the theoretical X-ray diffractograms of the JPCDS catalog of the $CdCl_2$ and $CdCl_2 \cdot H_2O$ phases (table numbers 09-0401 and 27-73, respectively). The analysis showed that diffraction patterns of all the obtained samples show diffraction peaks corresponding to cadmium hydrochloride $CdCl_2 \cdot H_2O$. For films, an increase in the relative intensity of the peak (020) was observed, which indicates the formation of a preferential orientation in the [010] direction.

The results of a precise calculation of the crystal lattice period indicate that in the studied cadmium chloride films, an increase in the periods **a** and **b** of the crystal lattice is observed in comparison with the theoretical data. At the same time, in the remaining batch, a decrease in these periods of the crystal lattice is observed. This is due to the fact that during the evaporation of the batch moisture firstly passes into the gas phase. As a result, the excess film is formed in the deposited film, and in the remaining batch, its depletion occurs.

To ensure the reproducibility of the thickness and phase composition of the cadmium chloride films, the following vacuum deposition technique was proposed. First, after several cycles of deposition, quartz resonator surface cleaning with ethanol was carried out. Secondly, prior to the deposition of a cadmium chloride film with a closed flap, the evaporated powder was calcined at an evaporator temperature of about 200°C. Calcination of the sample was carried out until the pressure in the chamber was restored at a level of 10-6 mm Hg. At the same time, all moisture was desorbed and pumped out of the volume of the working chamber, and evaporation of cadmium chloride was not observed.

After that the evaporation of the batch was carried out, for which the temperature of the evaporator rises to a temperature of 475°C, which ensures maximum use of the sample.

3.2 Study of the Process of «Chloride» Treatment of Cadmium Telluride Films

The X-ray diffraction pattern of CdTe films before the «chloride» treatment indicates their texturization. In this case, the presence of only two multiple diffraction maxima do not allow one to do an unambiguous conclusion about their phase composition. The diffraction peaks corresponding to the crystallographic planes (111) of the cubic modification and (002) of the hexagonal modification and the multiples thereof for cadmium telluride practically coincide. Doubles and packing defects, as the main defects of the crystal structure, accompany the formation of axial texture <111> bcc or <001> fcc crystal lattices.

The results of the investigation of the cadmium telluride surface before and after the «chloride» treatment are shown in Figure 1. A comparative analysis of surface morphology shows that as a result of the «chloride» treatment the fine-grained structure of cadmium telluride with grain size less than 1 μm is replaced by a coarse-grained structure with a size of up to 5 μm.

a

b

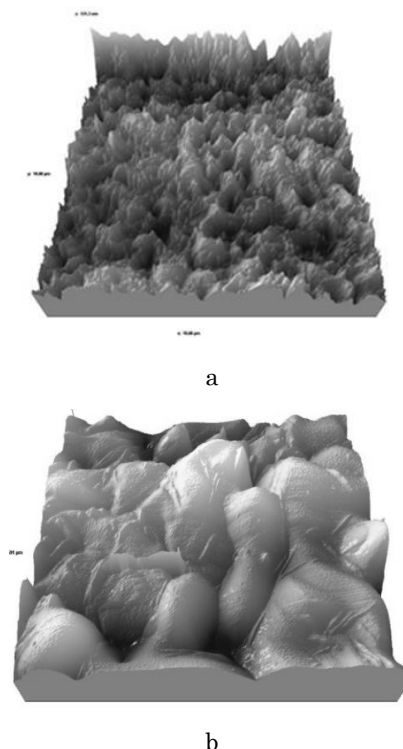**Fig. 1** – The morphology of the surface of CdTe layers 4.5 μm in thickness to (a) and after (b) «chloride» treatment identified with the Solver 47 atomic force microscope

According to the data of X-ray spectroscopy, after the «chloride» treatment of cadmium telluride layers, films of stable cubic modification are predominantly oriented in the thermodynamically equilibrium direction [422]. In the initial state, the columnar structure of cadmium telluride and the grain size are determined by the orienting action of a fine-grained film layer of cadmium sulphide of a hexagonal modification oriented in the [001] direction. After the «chloride» treatment from the back surface, the recrystallization of the base layer of CdTe begins, which leads to the disappearance of the cadmium sulphide layer orienting action on the structure of cadmium telluride films (Fig. 2).
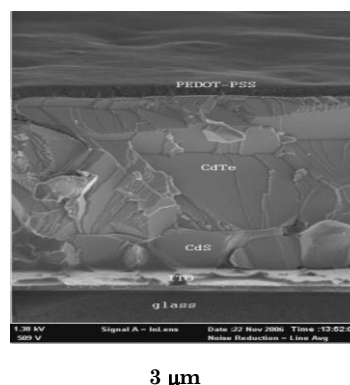

3 μm

Fig. 2 – The cross-section of the glass/ITO/CdS/CdTe heterosystem is visualized using a scanning microscope

The presence of a low-temperature eutectic in the $CdTe-CdCl_2$ system causes the conditions for recrystallization of the base layer to thermodynamically equilibrium, which causes the formation of an experimentally

observed coarse-grained structure predominantly oriented in the direction [422].Investigation of the cadmium telluride surface after deposition of the cadmium chloride layer showed that particles with cadmium chloride are observed on the surface at growth rates exceeding 0.1 μm per minute (Fig. 3, a).
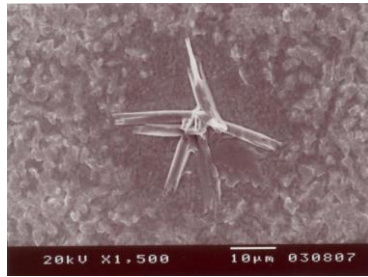
a
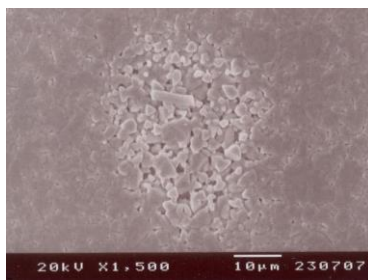
b

Fig. 3 – Microparticle $CdCl_2$ on the surface of CdTe after the «chloride» treatment (a), the place of shunting of the PEC caused by the presence of the $CdCl_2$ particle

If such particle forms on the surface of cadmium, then after the «chloride» treatment it decorates the surface (Fig. 3b) and causes the shunting of the instrumental structure, which sharply reduces the efficiency of the PEC. It was experimentally established that in order to minimize the formation of microparticles of cadmium chloride, it is necessary to limit the growth of the films to 0.1 μm per minute.

To optimize the thickness of cadmium chloride films, laboratory samples of the ITO/CdS/CdTe/Cu/Au PEC were studied for which a «chloride» treatment was carried out using layers of cadmium chloride (d_{CdCl2}) of various thicknesses. For the obtained of PECs, a measurement of light CVCs was carried out. By the analytical processing of the light current-voltage characteristics, the output parameters and the light diode characteristics were determined. For the study, a powder of cadmium chloride of 98 % purity was used. According to the published data, the main uncontrolled impurity in the initial batch was copper at the level of 1 %.

By the nature of the dependence of the efficiency on the light diode characteristics, several characteristic ranges of the thicknesses of the layer of cadmium chloride can be distinguished. The efficiency, output parameters and light diode characteristics of the samples that correspond to these ranges are given in Table 1.

Analysis of Table 1 shows that an increase in the thickness of cadmium chloride layer to 0.40 μm leads to an increase in efficiency to 9.5 % due to an increase in the open circuit voltage, the short-circuit current

Table 1 – Output parameters and light diode characteristics of the PEC ITO/CdS/CdTe/Cu/Au

Output parameters and light diode characteristics	layer thickness $CdCl_2$, μm			
	0.20	0.40	0.40*	0,60
J_c, mA/cm^2	19.8	21.1	17.1	19.7
U_{oc}, mV	640	734	795	643
FF, rel. units	0.58	0.62	0.63	0.64
Efficiency, %	7.4	9.5	8.6	8.1
J_f, mA/cm^2	19.9	21.1	17.3	19.8
R_s, Ohm·cm^2	2.8	5.0	5.6	3.0
R_{sh}, Ohm·cm^2	855	580	562	624
A, rel. units	2.8	2.0	1.9	2.4
J_0, A/cm^2	$4.4 \cdot 10^{-6}$	$3.6 \cdot 10^{-8}$	$1.3 \cdot 10^{-9}$	$5.3 \cdot 10^{-7}$

* - purity of cadmium chloride batch 99 %

density and the filling factor of the light current-voltage characteristic. The subsequent increase in the thickness of the of cadmium chloride layer to 0.60 μm leads to a decrease in efficiency to 8.1 % due to the decrease in the open circuit voltage and the short-circuit current density.

Simulation of the quantitative effect of light diode characteristics on the experimentally observed change in efficiency was carried out. For the simulation, the diode characteristics of the PEC with an efficiency of 7.4 % (thickness of cadmium chloride 0.2 μm) and with an efficiency of 9.5 % (thickness of cadmium chloride 0.4 μm) were chosen. For the first sample with a fixed set of four diode characteristics, the effect of the change in the experimentally determined range of values of the remaining diode characteristic on the efficiency was simulated. It is established that an increase in the efficiency from 7.4 % to 9.5 % with a set of diode characteristics determined from the experimental light CV characteristic can provide only the experimentally observed decrease in the density of the diode saturation current.

At the same time, the experimentally observed reduction in the efficiency from 9.5 % to 8.1 % (thickness of the cadmium chloride layer 0.6 μm) can also be modeled only by increasing the density of the diode saturation current. The change in the remaining diode characteristics does not have a significant effect on the experimentally observed change in efficiency. The decrease in the density of the diode saturation current indicates an improvement in the quality of the separating barrier and an increase in the lifetime of nonequilibrium charge carriers. Thus, at the cadmium chloride layer thickness 0.4 μm for PEC formed on the ITO layer, an efficiency gain of 9.5 % is due to optimization of the diffusion process and separation of the nonequilibrium charge carriers generated under the influence of light.

To study the effect of the batch purity of cadmium chloride, PEC samples were analyzed in which layers of cadmium chloride with a purity of 99 % were used. It was found that an increase in the purity of cadmium chloride leads to a decrease in efficiency, which is due to a decrease in the short-circuit current density (Table 1).

Simulation of the light diode characteristics effect on the efficiency has shown that the lower efficiency is due to a large series resistance and a smaller photocur-

rent. From our point of view, the presence of copper during chloride treatment leads to the generation of defective complexes of Cu_i-V_{Cd}. This defective complex, like the defective Cl_{Te}-V_{Cd} complex, is a stable acceptor, which increases the conductivity of the base layer of cadmium telluride and reduces the value of the series resistance.

The increase in the photocurrent density with the use of cadmium chloride batch with a high copper content is due to the possible segregation of interstitial copper, which is a small acceptor, on the grain boundary surface of cadmium telluride films. Stronger alloying of the grain boundary surface leads to the appearance of isotype *p+-p* transitions, the built-in field of which pushes the minority carriers into the grain volume, which reduces the rate of grain-boundary recombination, increases the lifetime and causes an increase in the photocurrent density.

The increase in the photocurrent density was confirmed experimentally in the study of the planar photocurrent distribution in the fabricated PEC. It was identified that when using cadmium chloride batch with a purity of 98 %, an increase in brightness is observed, which corresponds to an increase in the photocurrent. The analysis also showed that in the samples the maximum photo-sensitivity is observed at the center of the structure and falls off at the edges. In this case, there are inhomogeneities such as shunts (small areas of smaller photocurrent), which are randomly located on the surface of the PEC (see, for example, Fig. 4)
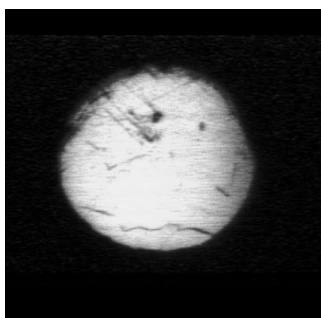

Fig. 4 – The distribution of the photocurrent (2D image) for the ITO/CdS/CdTe/Cu/Au PEC under illumination from the front

The presence of a region of collection of nonequilibrium charge carriers outside the contact (the contrast boundary of the circle) allows one to estimate the diffusion length, which is 1-2 μm.

3.3 Influence of the Substrate on the Modes of «Chloride» Treatment Conducting

In a number of studies (see, for example, [6]), it was established that the structural processes occurring in layers of cadmium telluride during the «chloride» treatment depend on its regimes for obtaining the base layer. Thus, in layers of cadmium telluride deposited at high substrate temperatures, there is no increase in grain size. To study the influence of the initial structure of the crystal structure of the base layer, we fabricated and studied the ITO/CdS/CdTe/Cu/Au instrumental structures on glass substrates with sublayers of sodium chloride. The results of studies of these instrument structures were compared with the results of the investigation of the ITO/CdS/CdTe/Cu/Au PEC on glass substrates.

The effect of the substrate on the crystalline structure of the base layer is due to its coefficient of thermal expansion (α). For glass, α is $9 \cdot 10^{-6} \, K^{-1}$, and for ITO layers it is $10 \cdot 10^{-6} \, K^{-1}$, for base layers of cadmium telluride it is $6 \cdot 10^{-6} \, K$. Therefore, when forming a CdS/CdTe-based PEC based on glass substrates, there are no problems associated with the difference in the coefficient of thermal expansion of the glass substrate and the film layers of the instrumental structure. However, if a layer of sodium chloride with $\alpha = 36 \cdot 10^{-6} \, K$ is deposited on a glass substrate, then there is a significant difference in the coefficients of thermal expansion.

The influence of the thickness of the of cadmium chloride layer on the efficiency of such instrumental structures as NaCl/ITO/CdS/CdTe/Cu/Au. was investigated.

The output parameters and light diode specific PEC characteristics NaCl/ITO/CdS/CdTe/Cu/Au are presented in Table 2.

Table 2 – Output parameters and light diode PEC NaCl/ITO/CdS/CdTe/Cu/Au characteristics

Output parameters and light diode characteristics	layer thickness $CdCl_2$, μm		
	0.05	0.10	0.15
J_c, mA/cm^2	8.8	17.8	17.0
U_{oc}, mV	536	678	633
FF, rel. units	0.47	0.53	0.36
Efficiency, %	2.2	6.4	3.9
J_f, mA/cm^2	10.0	18.0	18.2
R_s, Ohm·cm^2	11	6	5
R_{sh}, Ohm·cm^2	102	189	141
A, rel. units	2.9	2.8	3.0
J_0, A/cm^2	$4.8 \cdot 10^{-6}$	$2.2 \cdot 10^{-6}$	$3.6 \cdot 10^{-6}$

Analysis of Table 2 shows that the increase in efficiency with increasing thickness of the cadmium chloride layer to 0.10 μm occurs due to an increase in the open circuit voltage, the short-circuit current density and the filling factor of the light current-voltage characteristic. The subsequent increase in the thickness of the cadmium chloride layer to 0.15 μm leads to a decrease in efficiency primarily due to a decrease in the filling factor of the light current-voltage characteristic. Thus, for the NaCl/ITO/CdS/CdTe/Cu/Au PEC compared to the ITO/CdS/CdTe/Cu/Au PEC, the thickness of the cadmium chloride layers is characterized by the optimization of photoelectric processes after the «chloride» treatment.

In this case, the efficiency of the PECs formed on the sublayer of sodium chloride is also decreased in comparison with instrument structures formed on glass substrates without such sublayer.

Analysis of the quantitative effect of the light diode characteristics on the experimentally observed change in the efficiency of the NaCl/ITO/CdS/CdTe/Cu/Au PEC with a change in the thickness of the cadmium chloride layer showed that the decisive influence on the growth of the efficiency with an increase in the thickness of the cadmium chloride layer to 0.10 μm the values of the

diode saturation current density and the series resistance, as well as the growth of the shunting resistance. Decrease in efficiency at growth of a thickness of the cadmium chloride layer to 0.15 microns, according to results of modeling, is caused by growth of a diode saturation current.

A comparison of the light diode parameters shows that the high efficiency of the PEC without the sodium chloride interlayer is due to the lower density of the diode saturation current and the series resistance and the larger values of the shunt resistance (compare Table 1 and 2).

Comparative X-ray diffractometry studies of the base layers of cadmium telluride glass/NaCl/ITO/CdS/CdTe/Cu/Au PEC were carried out at a thickness of cadmium chloride of 0.10 μm and base layers of cadmium telluride ITO/CdS/CdTe/Cu/Au cadmium chloride 0.4 μm. In the base layers of the glass/ITO/CdS/CdTe/Cu/Au PEC after a «chloride» treatment, the direction of the preferential orientation changes from [111] to [422] is observed. The degree of preferential orientation in the [422] direction is 0.58. After the «chloride» treatment, the lattice period decreases from $\alpha = 6.509$ Å to $\alpha = 6.496$ Å and approaches the theoretical value $\alpha = 6.481$ Å.

The study of the degree of preferential orientation of the base layers of the glass/NaCl/ITO/CdS/CdTe/Cu/Au PEC of cadmium telluride layers indicates that, in comparison with instrument structures without a layer of sodium chloride, cadmium telluride layers are oriented in the direction of [311]. The degree of preferential orientation in the [311] direction is 0.74. The study of the lattice period of the base layers of the glass/NaCl/ITO/CdS/CdTe/Cu/Au PEC suggests that, in contrast to the instrumental structures without sodium chloride, it differs more from the tabulated value and amounts to $\alpha = 6.511$ Å.

Thus, the greater the density of the diode saturation current and the lower shunting resistance value of the glass/NaCl/ITO/CdS/CdTe/Cu/Au PEC there is a greater level of macrostresses, which is due to the significant differences in the coefficients of thermal expansion of the instrument structure and substrate. It should be noted that large macrostresses in the base layers of the instrumental structure caused the use of cadmium chloride layers of lower thickness to optimize photoelectric processes in the CdS/CdTe based solar cell during the «chloride» treatment, which reduced the effect of doping of the base layer and led to an increase in the series resistance.

4. CONCLUSIONS

The physical and technological foundations of reproducible «chloride» treatment of base layers of cadmium telluride by vacuum thermal evaporation of the cadmium chloride layer with subsequent annealing in air are developed. Before the evaporation of cadmium chloride, it is necessary to calcine the evaporated batch at a temperature of 200 °C to remove moisture, which can be checked by restoring the initial pressure in the vacuum chamber.

When depositing the cadmium chloride layer, it is necessary to limit the maximum growth rate of these films to 0.1 μm per minute, since in this case, the cadmium chloride macroparticles are not deposited on the surface of the base layer, the presence of which leads to the PEC shunting.

After several cycles of the cadmium chloride deposition, it is necessary to clean the surface of the quartz resonator, which, in case of high hygroscopicity of this material, it is reproducible to control its thickness by a quartz generator.

As a batch it is necessary to use cadmium chloride with a purity of 98 %, since at higher purity the efficiency of the PEC decreases because of the insufficient concentration of copper atoms in the base layers of cadmium telluride. The presence of copper leads to the generation of complexes of Cu_i-V_{Cd} possessing acceptor properties. This increases the electrical conductivity of the base layer and at the grain boundaries leads to the appearance of *p+-p* transitions, which reduces the rate of grain-boundary recombination.

It was experimentally determined that the optimum thickness of $CdCl_2$ during the «chloride» treatment and the efficiency of the CdTe-based PEC obtained at that time increases with a decrease in the level of macrodeformations in the base layer.

For the ITO/CdS/CdTe/Cu/Au PEC, the optimum thickness of $CdCl_2$ is 0.40 μm, and the efficiency is 9.6 %, and for NaCl/ITO/CdS/CdTe/Cu/Au PEC is 0.10 μm and 6,4 %.

The decrease in the initial level of macrodeformations in cadmium telluride films due to the decrease in free energy increases the thickness of the cadmium chloride film at which the liquid-phase recrystallization of the base layer occurs. Upon recrystallization, the lattice period approaches the reference value and the preferential orientation of cadmium telluride layers in the direction [422] is formed, which is characterized by the minimum density of twins and packing defects. As a result, the lifetime generated by the action of light nonequilibrium charge carriers increases, which causes the experimentally observed decrease in the density of the diode saturation current and the increase in the efficiency.

Физико-технологические основы «хлоридной» обработки слоев теллурида кадмия для тонкопленочных фотоэлектрических преобразователей

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Исследован процесс осаждения пленок хлорида кадмия при проведении «хлоридной» обработки базовых слоев теллурида кадмия для тонкопленочных фотоэлектрических преобразователей (ФЭП). Установлено, что для обеспечения воспроизводимости толщины и фазового состава пленок хлорида кадмия необходимо учитывать высокую гигроскопичность этого материала. Показано, что оптимальная скорость роста пленок хлорида кадмия составляет 0,1 мкм в минуту. При больших скоростях роста на поверхности базового слоя CdTe осаждаются макрочастицы хлорида кадмия, что вызывает шунтирование ФЭП в процессе «хлоридной» обработки. Определено, что после «хлоридной» обработки слоев CdTe наблюдается формирование крупнозернистой структуры, которая преимущественно ориентирована в термодинамически равновесном направлении [422]. При этом средний размер зерна возрастает до 5 мкм. Показано, что при проведении «хлоридной» обработки оптимальная чистота слоев хлорида кадмия составляет 98 % , что обусловлено легированием CdTe атомами меди. Недостаток меди при использовании более чистого хлорида кадмия снижает эффективность ФЭП за счет возрастания последовательного электросопротивления и снижения плотности фототока. Экспериментально определено, что оптимальная толщина хлорида кадмия при проведении «хлоридной» обработки и достигнутая при этом эффективность ФЭП зависит от применяемой подложки. Так для ФЭП ITO/CdS/CdTe/Cu/Au оптимальная толщина хлорида кадмия составляет 0,40 мкм, эффективность – 9,6 %, а для ФЭП NaCl/ITO/CdS/CdTe/Cu/Au – 0,10 мкм и 6,4 %, соответственно.

Ключевые слова: Фотоэлектрический преобразователь, Пленки теллурида кадмия, Хлорид кадмия, рентгеновская дифрактометрия, Световая вольт-амперная характеристика, Выходные параметры, Световые диодные характеристики.

Фізико-технологічні основи «хлоридної» обробки шарів телуриду кадмію для тонкоплівкових фотоелектричних перетворювачів

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Досліджено процес осадження плівок хлориду кадмію при проведенні «хлоридної» обробки базових шарів телуриду кадмію для тонкоплівкових фотоелектричних перетворювачів (ФЕП). Встановлено, що для забезпечення відтворюваності товщини і фазового складу плівок хлориду кадмію необхідно враховувати високу гігроскопічність цього матеріалу. Показано, що оптимальна швидкість росту плівок хлориду кадмію становить 0,1 мкм в хвилину. При великих швидкостях зростання на поверхні базового шару CdTe осідають макрочастки хлориду кадмію, що викликає шунтування ФЕП в процесі «хлоридної» обробки. Визначено, що після «хлоридної» обробки шарів CdTe спостерігається формування крупнозернистої структури, яка переважно орієнтована в термодинамічно рівноважному напрямку [422]. При цьому, середній розмір зерна зростає до 5 мкм. Показано, що при проведенні «хлоридної» обробки оптимальна чистота шарів хлориду кадмію становить 98 %, що обумовлено легуванням CdTe атомами міді. Недолік міді при використанні більш чистого хлориду кадмію знижує ефективність ФЕП за рахунок зростання послідовного електроопору і зниження щільності фотоструму. Експериментально визначено, що оптимальна товщина хлориду кадмію при проведенні «хлоридної» обробки і досягнута при цьому ефективність ФЕП залежить від застосовуваної підкладки. Так для ФЕП ITO/CdS/CdTe/Cu/Au оптимальна товщина хлориду кадмію становить 0,40 мкм, ефективність - 9,6 %, а для ФЕП NaCl/ITO/CdS/CdTe/Cu/Au - 0,10 мкм і 6,4 %, відповідно.

Ключові слова: Фотоелектричний перетворювач, Плівки телуриду кадмію, Хлорид кадмію, Рентгенівська дифрактометрія, Світлова вольт-амперна характеристика, Вихідні параметри, Світлові діодні характеристики.

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