Thin films CdS/CdTe solar cells with different activation processes base layer

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Abstract. Shown in this work is the possibility to create industrial technology for production of solar cells FTO/CdS/CdTe. The technology includes annealing in freon processing step for activation of cadmium telluride base layers deposited by thermal vacuum evaporation. Solar cells with efficiency of 7% have been obtained. Structural and morphological researches allowed to identify interrelation between photovoltaic characteristics and features of the recrystalization process in base layers after annealing in freon as compared with the standard chloride treatment.

Keywords: solar cells FTO/CdS/CdTe, freon, recrystalization.

1. Introduction

One of the main technological operations in production of high-performance thin film solar cells (SC) of CdS/CdTe base is chloride treatment, which leads to optimization of photovoltaic processes [1]. Without chloride treatment CdS/CdTe SC has a low efficiency related with a low photocurrent. Under chloride treatment, $CdCl_2$ layer is deposited onto CdTe surface by laser [2], which is followed by thermal evaporation [3] or chemical bath deposition [4] and then annealing in air for 10–30 min [5]. The optimum time, annealing temperature and $CdCl_2$ thickness are empirically obtained and have wide dispersion. At the finish step of chloride treatment, the remains of $CdCl_2$ and products of chemical reaction are removed from the surface of base layer by water cleaning or etching in bromine-methanol solution.

The chloride treatment leads to 3 to 6-fold increasing the SC efficiency [1]. It is related with growth of grains sizes in CdTe and CdS [6], decrease in the specific resistance of base layer [7]; growth in lifetime of non-equilibrium minor charge carriers [8], change in the mechanism of charge transport [9]. Structural changes occurring after chloride treatment stipulate the recrystallization process in cadmium telluride, since the eutectic temperature of $CdTe-CdCl_2$ system is (490 ± 5) °C. Intensive search of other alternative more

technological methods of chloride treatment (see, for example, [10]) are being performed now. With application of annealing in argon and freon atmosphere the CdTe layers deposited using close space sublimation (CSS) method, the device structure with the efficiency 15.8% was formed [11]. The CSS method is difficult for adaptation in industrial production, because high temperatures of substrate (~550 °C) and significant speeds of deposition (~100 Å/s) as well as application of complicated monitoring systems to obtain planar uniformity of deposited layers are needed. Now high-performance CdS/CdTe SC are obtained by such economic industrial method as the thermal one. However, applied in manufacturing these devices was the standard chloride treatment. Therefore, to create industrial technology of thin film SC on CdS/CdTe base, the comparative researches of device structures obtained using the thermal vacuum evaporation method and subjected to standard chloride treatment as well as treatment in freon vapor are topical.

2. Experimental

For fabrication of thin film SC FTO/CdS/CdTe/Cu/Au in a single cycle by using the PVD method, layers of CdS and CdTe were deposited on a glass substrate coated with fluorine doped tin oxide (FTO). The CdS layer with

the thickness 0.4 μm was grown at the substrate temperature close to 150 °C. The CdTe layer of the thickness 4 μm was grown at the substrate temperature of 300 °C.

Two different activation processes, namely: the standard chloride treatment and freon treatment were applied to this device heterostructure. At standard chloride treatment, the $CdCl_2$ layer thickness 0.1–0.6 μm was grown on CdTe surface by thermal evaporation. Then, annealing in air at the temperature of 430 °C for 30 min was applied. At freon treatment, the device heterostructure was kept in a silica ampoule with atmosphere Ar+15% HCF_2Cl at pressure 100 mbar and annealed at the temperature 400 ºC for 1 to 20 min. It is necessary to note that CdTe layers deposited by CSS method and annealed in the above gas composition [11] possessed the highest efficiency.

After both activation processes of the base layer, the surface of cadmium telluride was etched in bromine-methanol solution to remove products of chemical reaction and to create a thin tellurium layer. The back contacts were made using evaporation of Cu/Au layers with 10- and 50-nm thickness, accordingly, followed by short annealing at 200 °C in air.

Under AM1.5 illumination, the light current-voltage ($I - V$) characteristic of device was measured and output parameters: short current density (J_{sc}), open circuit voltage (U_{oc}), fill factor (*FF*) and efficiency (η) were obtained.

In accordance with the equivalent curcuit to the SC [12], for quantitative descriptions of photo-electric processes there used are light-diode characteristics: the density of diode saturation current (J_0), the density of photocurrent (J_{ph}), the ideality coefficient of the diode (*A*), the successive resistance (R_s) and shunting resistance (R_{sh}). Relation of the efficiency and initial SC parameters with diode characteristics is set by the theoretical expression for light $I - V$ characteristic of SC [12]:

$$J = -J_{ph} + J_0\{\exp[e(U - JR_s)/(AkT)] - 1\} +$$

$$+ (U - JR_s)/R_{sh} , \qquad (1)$$

where *J* is the density of loading current; *e* – electron charge; *k* – Boltzmann constant; *T* – temperature; *U* – voltage of loading.

The light-diode characteristics and efficiency of SC were determined using computer approximation of experimental light $I - V$ characteristic in accord with the theoretical expression (1) [13]. Thus, the efficiency calculated using the theoretical light $I - V$ characteristic (1) and that measured experimentally coincide with the accuracy 0.01%.

The method of X-ray diffraction was applied to investigate structural features of SC base layers. In the investigations, the diffraction spectrum obtained at continuous 2θ-scanning within the interval of angles 2θ = 20…70° with focusing by Bragg-Bretano in radiation of the copper anode was used.

The preferential orientation of films was determined using analytical processing the diffraction peaks, which enabled us to obtain the maximum texture coefficient C_i [14]:

$$C_i = \frac{NI_i}{I_{0i} \sum_{i=1}^{N} I_i / I_{0i}} , \qquad (2)$$

where I_i is the intensity of detected *i* peak; I_{0i} – intensity of the same *i* peak in accord to ASTM tables; *N* – number of diffraction peaks detected at the analysis (the reflections that correspond to different indexes were not taken into account). For comparison of samples on a texture degree, the parameter *G* was calculated [14]:

$$G = \sqrt{N^{-1} \sum_{i=1}^{N} (C_i - 1)^2} . \qquad (3)$$

The precise determination of the lattice constant for base layer of cadmium telluride was performed using the extrapolation function $(\cos^2\theta/\sin\theta) + (\cos^2\theta/\theta)$ [14]. The methods of a scanning electronic and atomic tunneling microscopy were applied to investigate surface morphology.

3. Discussion

The light current-voltage characteristics of SC obtained without any chloride treatment and with application of the standard chloride treatment and freon treatment are shown in Fig. 1. The output parameters and light diode characteristics are adduced in Table 1. We can see that after the standard chloride treatment and after freon treatment there is an essential improvement of SC efficiency, however, the freon treatment gives smaller effect. The lower efficiency of SC obtained using the freon treatment is stipulated by a low value of the open circuit voltage. It is related to poor quality of the separation barrier, which demonstrates a high value of the diode saturation current density J_0 (see Table 1). As follows from Table 1, the other diode SC parameters kept the same level. It is reasonable to assume that poor quality of the separation barrier is a result of difference in crystalline and energy structures of the base layer at different kinds of treatment. The series of structural investigation to check this assumption was conducted.

The investigation of surface morphology of as-deposited layers of cadmium telluride has shown that grain size lies within the range 0.5–1 μm and structure of layers is very dense (Fig. 2a). After chloride treatment, the changes in the shape and sizes of grains are observed (Fig. 2b). The grains boundaries are unification and the size of grains is incremented up to 2–5 μm. At the same time, inside some large grains inner boundaries are visualized. The density of layer is decreased.

After annealing in freon, the size of grains is increased, and grain boundaries also start to be integrated (Fig. 2c), however, these processes are less pronounced. The microphotographs of surface of layers

subjected to annealing in freon for 5 and 10 min are shown in Fig. 3. The analysis shows that after annealing for 5 min recrystallization of the base layer was not completed yet. After annealing for 10 min, the size of grains becomes larger. The shape of cadmium telluride grains after annealing in freon as compared to the standard chloride treatment is more stable.
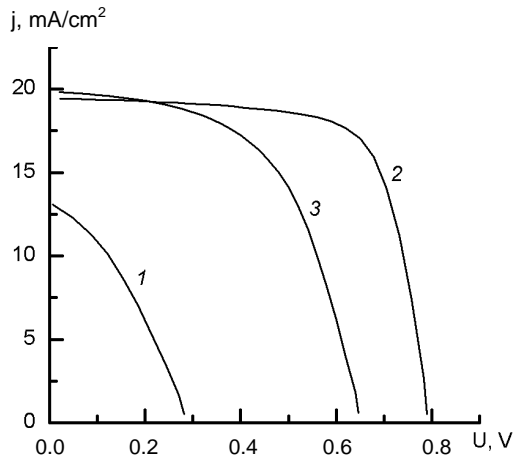
Fig. 1. Light voltage-current characteristics of solar cells without chloride treatment (*1*), after standard chloride (*2*) and after freon treatments (*3*).
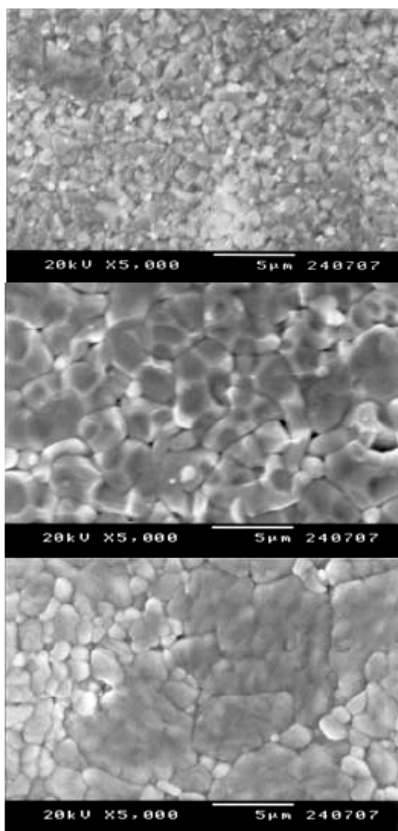
Fig. 2. Microphotographs of surface of cadmium telluride layer: a) as-deposited layers, b) after chloride treatment, c) after annealing in freon.
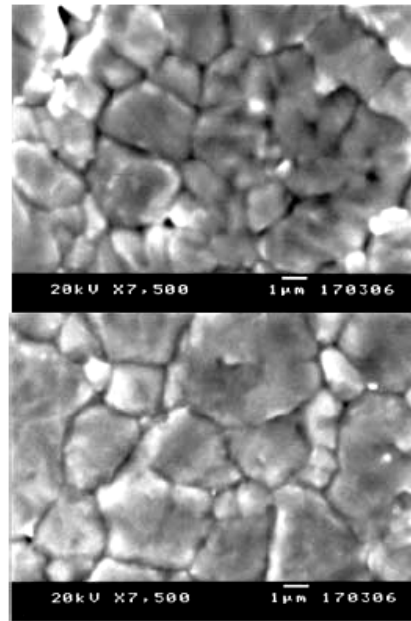
Fig. 3. Influence of annealing time in freon on morphology of surface of cadmium telluride layers: a) time of annealing 5 min, b) 10 min.

The investigations of surface relief by using the method of atomic force microscopy testify to decreasing the surface relief both in the process of chloride treatment and when annealing in freon. Thus, the surface relief decreases to lesser degree when processing in freon.

The influence of activation processes on the direction and preferential orientation degree as well as lattice constant of the base layers was investigated using X-ray diffraction methods (Table 2). It is ascertained that as-deposited layers of cadmium telluride are oriented in the direction ⟨111⟩, which is characterized by the maximum growth rate. The layers deposited in non-equilibrium conditions grow in this direction. The grains of cadmium telluride oriented in this direction contain a high concentration of twins and defects of packing, which essentially limits the efficiency of photoelectric processes, because of the increase in velocity of volume recombination of non-equilibrium charge carriers. The lattice constant in these layers is 6.499 Å. As the theoretical value of this constant is 6.481 Å, it becomes apparent that the as-deposited layers of cadmium telluride experience considerable macro-deformation caused by 10% difference in lattice constants of CdS and CdTe layers as well as difference in thermal expansion of a glass substrate and deposited layers ($\alpha_{CdTe} = 6 \times 10^{-6}\,K$, $\alpha_{glass} = 9 \times 10^{-6}\,K$). Thus, up to chloride treatment the efficiency of FTO/CdS/CdTe/Cu/Au SC is limited by a high density of defect packing and twins, and considerable macro-deformations in the base layer of cadmium telluride, as well.

Table 1. Output parameters and light diode characteristics of SC with different types of back contacts in deposited state.

Output parameters and light diode characteristics	Traditional chloride treatment	Processing in freon
J_{sc}, mA/cm^2	19.58	19.92
U_{oc}, mV	795	647
R_{sh}, Ohm·cm^2	570	459
R_s, Ohm·cm^2	1.8	1.4
FF, relative units	0.711	0.560
J_0, A/cm^2	4.12×10^{-10}	2.06×10^{-5}
J_{ph}, mA/cm^2	19.64	20.01
A, relative units	1.76	3.71
η, %	11.07	7.2

Table 2. Influence of activation technology on the crystalline structure of base layer of FTO/CdS/CdTe/Cu/Au film SC.

Structural characteristics	Direction of preferential orientations	Degree of preferential orientation G	Lattice constant a, Å
after deposition	$\langle 111 \rangle$	0.29	6.499
chloride treatment	$\langle 422 \rangle$	0.85	6.446
annealing in freon 5 min	$\langle 422 \rangle$	0.66	6.488
annealing in freon 10 min	$\langle 422 \rangle$	0.79	6.487

It is established that at chloride treatment the efficiency more than 11% is reached at the thickness of $CdCl_2$ layer 0.6 μm. This heat treatment causes changes in orientation of the base layers. After recrystallization, the CdTe layers have the main orientation in direction $\langle 422 \rangle$. This direction corresponds to equilibrium agreement of growth. The lattice constant of the layers is reduced down to 6.466 Å.

Lowering the lattice constant of the base layer down to values smaller than the theoretical ones for cadmium telluride is caused by creation in it of an intermediate layer of solid solutions $CdS_x Te_{1-x}$ near to the interface boundary. Creation of solid solutions at the boundary CdS/CdTe reduces difference in lattice constants of contacting layers. Lowering the level of macro-stresses incipient because of differences in coefficients of thermal expansion of substrate and cadmium telluride layer is promoted by recrystallization of the base layer, which starts at the boundary $CdCl_2$-CdTe.

It is ascertained that under annealing in freon the highest efficiency does not exceed 7% and is reached after heat treatment for 10 min. When annealing in freon as well as after chloride treatment, the layers of cadmium telluride will be mainly oriented in direction $\langle 422 \rangle$. However, preferential orientation degree is lower

(see Table 2). It is related that the eutectic recrystallization does not happen, and the size of grains is incremented by recrystallization processes. The lattice constant of layers is reduced down to 6.488 Å. It indirectly testifies that under annealing in freon the solid solutions at the boundary of CdS-CdTe are formed less intensively. Under standard chloride treatment, the presence of sufficient quantity of chlorine at the interface boundary leads to diffusion of sulfur in CdTe layer, which promotes formation of solid solutions [15]. The availability of chlorine at the interface boundary is conditioned by the fact that, under chloride treatment of the cadmium chloride layer deposited on surface of cadmium telluride, the subsequent annealing promotes intensive grain boundary diffusion of chlorine into the region of interface boundary CdS-CdTe, when recrystallization front moves. If processing in freon, diffusion happens from the gas phase, and maybe it is limited by reaction of formation of chlorine compounds on the surface of base layer.

4. Conclusions

For the first time, the FTO/CdS/CdTe SC with efficiency 7% have been obtained by annealing the CdTe base layer in freon at 400 °C for 10 min, this layer being deposited using thermal vacuum evaporation. It proves the possibility to create industrial technology of these device structures with the offered operation for base layer activation.

It is established that the lower efficiency of designed SC is caused by a greater density of diode saturation current that is related to features of the recrystallization process in base layers as compared to processes of recrystallization taking place when realizing the standard chloride treatment.

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