Adopting of DC Magnetron Sputtering Method For Preparing Semiconductor Films

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***Abstract*— It has been carried out the experimental studies of the process of cadmium telluride magnetron sputtering with direct current, and the impact of a magnetron sputtering mode on CdTe films crystalline structure. In order to create thin-film solar cells based on cadmium sulfide and telluride CdTe films for the base layers of thin film solar cells was obtained on flexible polyimide substrates by magnetron sputtering with direct current for the first time. It has found that increasing the magnetron discharge current up to 80 mA leads to increase in coherent scattering regions what is due to an increase in the thickness of the cadmium telluride films of the hexagonal modification having a columnar structure.**

Keywords*— flexible solar cells based on cadmium sulfide and telluride, method of magnetron sputtering with direct current, thermoelectronic emission, target

I. Introduction

Thin film solar cells (SC), based on cadmium sulfide and telluride, represent an alternative to the most widespread silicon crystalline solar cells in the capacity of autonomous sources of electric energy in terrestrial and space conditions. Modern high efficiency film SC based on CdS/CdTe are produces in the back configuration on the glass substrate through which solar radiation enters the base layer [1]. In terrestrial conditions, SC based on CdS/CdTe, in accordance with the optimum band gap of cadmium telluride, have the greatest efficiency – 29 %. In space applications, due to the nature of the chemical bonds of CdTe such SC are the most resistant to radiation [2]. In addition, lower material and energy consumption of manufacturing process of film photovoltaic converters based on CdS/CdTe provides a lower cost compared to crystalline silicon photovoltaic converters. For example, in the conditions of industrial production, First Solar company which manufactures photovoltaic converters based on CdS/CdTe said about reaching "grid parity" when the cost of electricity produced by photovoltaic converters equals the cost of electricity produced by conventional power sources [3]. It should be note that conventional SC based on CdTe essentially concede to SC based on crystalline silicon in power density (value of electric power generated per unit weight of a SC).

Substitution of glass substrates, which are conventional for SC based on CdS/CdTe to a flexible substrate, allows the reduced power to increase by several orders of magnitude, and to surpass by this parameter not only silicon-based SC, but also SC based on A_3B_5. However, in addition, due to the lower thermal stability of the polyimide substrate it is necessary to reduce the deposition temperature of the cadmium telluride films below 400 °C what is impossible for methods of close-spaced sublimation [4,5] and vapor phase transport deposition [6, 7] which are conventionally used to produce high performance SC based on CdS/CdTe. When implementing these methods forming the base layer of cadmium telluride has carried out at a deposition temperature of 550 °C.

Low temperature techniques for production of cadmium telluride films that can be realize in mass production includes magnetron-sputtering method [8]. The main technological challenge of getting the semiconductor films by magnetron sputtering with direct current is a low rate of film growth. This is because during sputtering, a low-conducting substrate accumulation of positive charge takes place, and this charge does not have time to drain off. This creates a counter field inhibiting the argon ions which bombard the substrate what causes a decrease in the discharge current. Also for materials with a high work function of electrons, which include most semiconductors and dielectrics, a low electron emission is characteristic. Accordingly, when the DC sputtering method was implement for semiconductor materials, low ion current densities are observes that do not allow the realization of the production of thin films of semiconductors in industrial scale.

Therefore, obtaining of cadmium telluride films for base layers of flexible SC by magnetron sputtering with direct current is an urgent technological problem for which solution experimental studies of the process of cadmium telluride magnetron sputtering with direct current and of the impact of the magnetron sputtering modes on the crystalline structure of CdTe films was carry out.

This problem can been solved by increasing the discharge current density during DC magnetron sputtering of cadmium sulfide and telluride due to the use of the phenomenon of thermionic emission providing enhanced ionization of the working gas.

II. Experimental Technique

The mentioned problem can been solved due to the intensification of thermionic emission when the cadmium telluride target surface is preheated up to a 166 °C and then maintained in the range from 156 °C to 166 °C. For this temperature interval, the increase of discharge current due to thermionic emission exceeds the effect of reducing the discharge current due to the growth of working gas ions with the target surface atoms elastic collisions probability. The heating of the target was carry out by the heater combined with a substrate heater placed above magnetron surface using an automated negative feedback based on a microcontroller controlling the heater and providing stabilization of the discharge current with an accuracy of ± 2 mA with constant voltage on the magnetron and argon pressure.

In the work, we have used deposition of cadmium telluride films by magnetron sputtering with direct current. We used an experimental vacuum plant VUP-5M with original magnetron systems what important design feature was their cooling circuit which includes only a magnetic system. The manufacturing of target provided by cold pressing from cadmium telluride powder and with diameter - 76 mm, and thickness – 2 mm. Target cold pressing pressure was 100 MPa. The dwell time of the target at this pressure was 15 hours. After pressing the target its vacuum annealing has performed at a residual pressure of at least 10^{-4} mmHg and a temperature of 80 °C. When depositing CdTe layers thermostable polyimide film manufactured by Upilex firm with thickness up to 10 microns has used in the capacity of a substrate. The flexible substrate has positioned in a movable substrate holder of VUP-5M vacuum chamber in close contact with the front surface of the thermocouple. Before the process of applying the cadmium telluride layers pumping in the working volume to a pressure of 10^{-5} Pa has carried out. Argon puffing in the capacity of a working gas has carried out using an automated puffing system SNO.

To realize the effect of thermionic emission in the DC magnetron sputtering of cadmium telluride, we used a heated cathode, which produce additional electrons mainly by thermionic rather than secondary emission.

During studying the process of DC magnetron sputtering to produce cadmium telluride films, five processing regimes were realize. These regimes differed by argon pressure (P_{arg}), voltage on the magnetron (V), and the heating modes of the substrate and target also, we measured the dependence of the discharge current of the magnetron (I) on the sputtering time (t).

III. Results and their Discussion

It has been find that during the magnetron sputtering of a cadmium telluride target, a change in the discharge current was observe. When the first mode was realize, firstly the preheating of the substrate to a temperature of 200 °C was carry out with the magnetron turned off (Fig. 1a). In this case, the substrate was remove from the magnetron. Then, a voltage of 800 W was apply to the magnetron, the argon pressure was 2.5 Pa, and after that, the substrate transferred to a position above the magnetron (Fig. 1b). Measurement of the discharge current versus sputtering time shows that during the first 4 minutes of sputtering the discharge current did not exceed 1.2 mA. It was visually establish that, at this discharge current, a cadmium telluride film on the surface of the flexible substrate has not formed, since the sputtering of the target did not occur. However, from 4 up to 8 minutes of sputtering, the sputtering current was increased up to 60 mA (Fig.2, curve 1) and then did not change during the subsequent sputtering time.

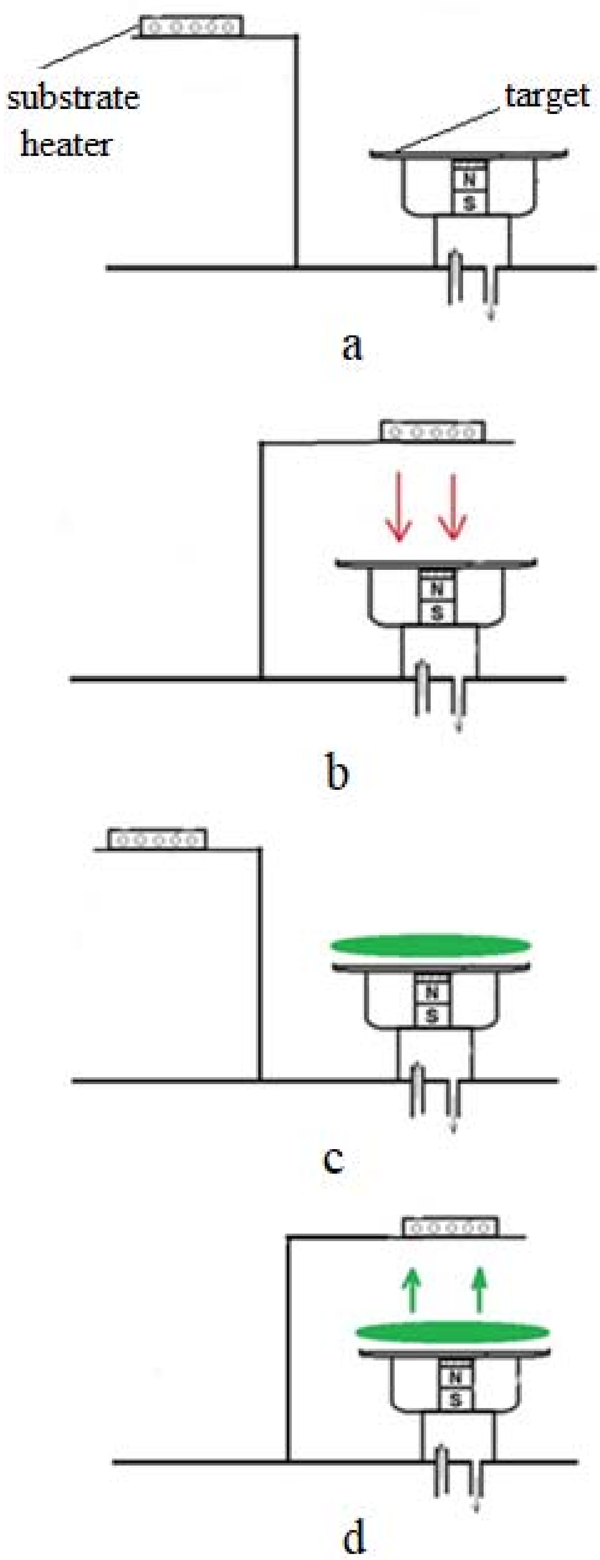

Fig. 1. Mutual orientation of the magnetron and the substrate at various stages of cadmium telluride film deposition regimes realization: substrate heating (a); heating of sputtered target (b); increase of disharge current during

target sputtering due to thermionic emission effect (c); sputtering regime with increased discharge current (d)

At the same time, active formation of cadmium telluride film was visually observes on the substrate surface. When the second mode was realized, simultaneously with the beginning of the substrate heating, which was located away from the magnetron, a voltage V = 600 V was applied to the magnetron at P_{arg} = 2 Pa (the procedure of target training - Fig. 1c). The preheating temperature of the target was 200 °C. Then, without interrupting the magnetron discharge, the substrate transfers to a position above the target (Fig. 1d). It was establish that the process of magnetron sputtering began at the initial discharge current of 3.1 mA.

When the sputtering time increased up to 4 minutes, a growth of discharge current up to 20 mA was observes experimentally, then, with a further increase in the sputtering time up to 8 minutes, the discharge current growth up to 85 mA (Fig.2, curve 2). With a further increase in the sputtering time from 8 minutes to 20 minutes, a slight decrease of current on 10 % was observes.

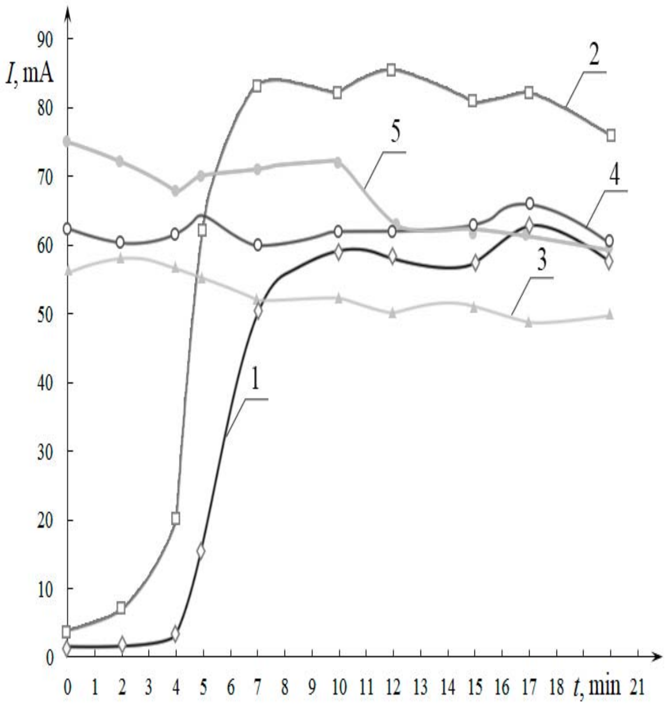

Fig. 2. Graphs of discharge current versus sputtering time for various variants of realized technological processes

When the third regime was realized at the position where the substrate was removed from the magnetron (Fig. 1a), it was firstly heated to 200 °C, then during 3 minutes the substrate was heated in the position above the magnetron (Fig. 1b). After that, a voltage of 600 V was supply to the magnetron at the argon pressure on 1.8 Pa (Fig. 1d). Such changing of process conditions led to an increase of the initial discharge current up to 55 mA. During the sputtering process, a slight monotonic decrease of the discharge current up to 50 mA was observes (Fig.2, curve 3).

In comparison with the third technological regime, at the realization of the fourth regime, the substrate heating temperature both on the opposite from magnetron side and above the magnetron surface was increase up to 230 ºC. The magnetron was supply by voltage of 600 V at an argon pressure of 1.7 Pa. As a result of this regime, the initial discharge current increased up to 62 mA. During the sputtering process, a slight monotonic decrease of the discharge current up to 60 mA was observes (Fig.2, curve 4).

When the fifth mode was realize, the substrate heating temperature was increase up to 240 °C, and the preheating time of the substrate above the target surface was up to 5 minutes. This led to an increase of initial discharge current up to 75 mA at a voltage of 600 V and an argon pressure of 1.5 Pa. During the sputtering process, a monotonic decrease of the discharge current up to 60 mA was observes (Fig.2, curve 5).

A carried out study of DC magnetron sputtering process of cadmium telluride target showed that the change of magnetron sputtering current during the deposition of cadmium telluride film is related to the heating of the of the target material surface. Experiments show that this can be due to thermal radiation from the substrate surface. Indeed, it has been experimentally show that with increasing substrate temperature and, primarily, the time of its heating above the target surface, an increase of the initial discharge current from 1.2 mA up to 75 mA has been observes. The temperature of the target surface can also be increase by growing the time of magnetron sputtering by bombarding the target with ions of the working gas. This is confirms indirectly by the presence of discharge current rapid growth areas from the discharge time (see curves 1 and 2 on Fig. 2). In order to test the hypothesis, we measured the temperature of the target surface during the realization of second regime (Fig. 3).

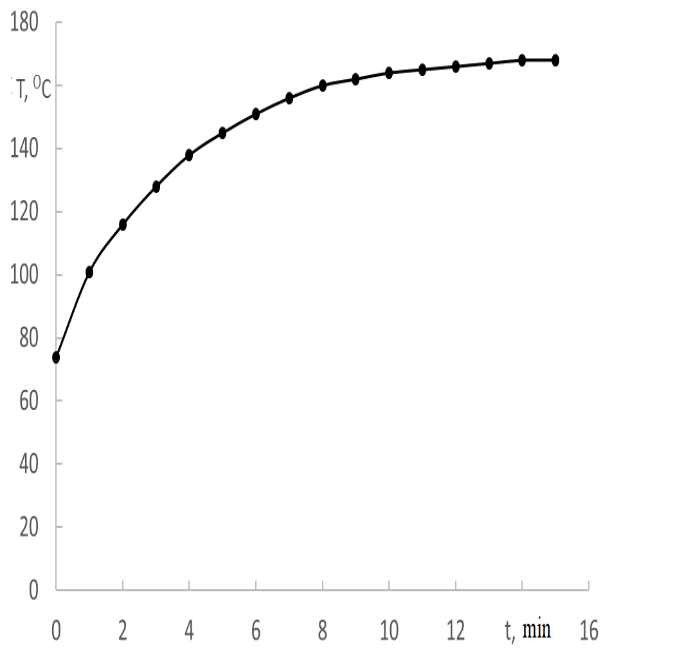

Fig. 3. Dependence of sputtered target temperature from the sputtering process duration.

During the temperature measurements, we disconnect the power supply of the magnetron, which led to the disappearance of the plasma, the presence of which distorts the results of electrical measurements. As can be seen (Fig. 3), the character of the change in temperature coincides with the change of current. When we reached the temperature up to 156 ºC on 7 minutes, the discharge current increased up to 83 mA, which corresponds to beginning of target intense sputtering. During the subsequent sputtering time, temperature increased by only on 12 °C, and the discharge current was reduce up to 77 mA. Thus, the heating of the target surface up to 156 °C causes an increase of secondary electrons thermal emission intensity from the target surface to the magnetron discharge zone, which leads to a decrease of target electrical resistance as a result of the main charge carriers thermal generation. An increase of secondary electrons concentration increases the probability of argon molecules ionization, which in turn intensify the bombardment of the target surface with argon ions and, accordingly, leads to increase the target sputtering rate. When the temperature of the target is increase up to 168 °C, the discharge current was reduce up to 77 mA. Consequently, with the growth of the target temperature, two competing processes are observes: an intensification of thermionic emission and an increase of elastic collisions probability. Therefore, depending on the physical nature of the target material, the first and second process may be predominant. For cadmium telluride in the target temperature range from 156 °C to 166 °C, the intensification of thermionic emission has a greater effect on the magnitude of the ion current than the increase of elastic collisions probability. At a temperature value 166 °C, the maximum discharge current up to 85 mA was observes. When target heated above 166 °C, the decisive influence on the discharge current was exerts by the increase of elastic collisions probability, and therefore the emission current decreases, which was observes experimentally.

IV. Conclusions

For the first time, the cadmium telluride films by thickness of 1-5 μm have been produce on flexible polyimide substrates by direct current magnetron sputtering. This process realized due to heating the target surface to intensify the thermal emission of the secondary electrons in the magnetron discharge zone and to reduce the electrical resistance of the target as a result of thermal generation of main charge carriers.

The obtained experimental data make it possible to propose the following method for the realization of deposition of cadmium telluride or other semiconductor materials films by the method of direct current magnetron sputtering. The surface of magnetron target, whose design allows the target to be cools, is heating up to a temperature of 166 °C, which corresponds to the maximum discharge current.

To heat the target, a substrate heater placed above the magnetron's surface. After reaching a temperature of 166 °C is supplied with a discharge voltage and the process of sputtering the target begins during of which the automated feedback system maintains the target temperature in the range from 156 °C to 166 °C in which the thermionic emission effect increases the discharge current and intensify the process of cadmium telluride sputtering.

The proposed method makes it possible to obtain high-quality films with a high growth rate by a well-developed industry and an economical method of magnetron sputtering with direct current and does not require making significant changes to the design of typical magnetron sputtering plants.

The practical realization of proposed method in industrial scales will be allow to increase the values of thin film solar cells production, especially the solar cells based on flexible polyimide substrates.

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