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Physical and Technical Conditions of Cadmium Sulfide and Cadmium Telluride Films Deposition in a Quasiclosed Space for Flexible Photoelectric Converters

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Abstract: The experimental studies of critical condensation temperatures during the deposition of cadmium sulfide and cadmium telluride films in a quasi-closed volume made it possible to determine the modes in which precipitation occurs under the conditions close to thermodynamically equilibrium ones and at substrate temperatures below the thermal destruction temperature of the polyimide films by Upilex company. The technological equipment adapted to vacuum equipment of electronics industry domestic enterprises was developed for the technical realization of these conditions. This equipment allows the sequential deposition of sulphide and cadmium telluride layers in a single technological cycle by condensation from a quasi-closed volume under the conditions close to thermodynamic equilibrium ones. At a deposition temperature of 434°C on polyimide substrates with an ITO film layer on the surface of which a nanoscale ZnO interlayer is located, CdS layers were obtained with the thickness of 0.3 μm of a stable hexagonal modification. On the surface of CdS layers at the temperatures below 440°C, CdTe layers were developed with the thickness of 4 μm of a stable cubic modification. The approbation of the CdS/CdTe heterosystems in the composition of flexible photoelectric converters shows that with the increase of cadmium telluride deposition temperature from 353-439°C, the efficiency ratio of these instrument structures increases from 10.5-12.2% which is caused by the short-circuit current density increase from 21.2-21.9 mA/cm^2, no-load voltage from 788-820 mV and the filling factor of the light-volt-ampere characteristic from 0.625-0.680.

Key words: Cadmium sulfide and cadmium telluride films, deposition in a quasi-closed volume, substrate temperature, the conditions close to thermodynamically equilibrium ones, flexible photoelectric converters

INTRODUCTION

Currently the efficiency of 22.1% is achieved for Film Photoelectric Converters (FPC) based on sulfide and cadmium telluride films of the rear configuration. Such instrument structures were obtained by "first solar" company on glass substrates by the steam transport method (VTD method) using the deposition temperatures above 500°C. The achievement of FPC high efficiency is conditioned by the realization of deposition regimes close to thermodynamically equilibrium ones.

Taking into account the achieved efficiency and the low energy intensity, CdS/CdTe based film FPC represent an alternative of FPC based on mono-Si and GaAs (Kumar and Rao, 2014; Scholten, 2013). The replacement of glass substrates with polyimide films makes it possible to create flexible FPC with the record values of electrical power per unit of weight. These qualities of flexible FPC provide broad prospects not only for their space but also for their terrestrial application. In particular they can be used as the power sources for unmanned aerial vehicles, autonomous power sources for radioelectronic equipment, power supplies for air conditioning systems of cars and boats, photovoltaic batteries that are mounted on the roofs of houses with complex surface profiles, etc.

At present, apical, kapton, kaptrex, meldin, vespel, plavis and UPILEX companies produce heat-resistant transparent polyimide films. The highest thermal stability up to 450°C is provided by UPILEX-S polyimide films. The average transmittance ratio reaches 80% for these films in a visible region which makes them the most promising ones for the creation of highly efficient flexible FPC of the

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rear configurations. However, the limitation of film thermal stability at 450°C does not allow to use them as substrates for the deposition of cadmium telluride by the steam transport method. The vacuum method of cadmium telluride condensation in a Quasi-Closed Area (QCA) like VTD, allows to perform the deposition under conditions close to thermodynamic equilibrium ones (Bubnov *et al*., 1975). Proceeding from this, the main task of this study will be to determine the conditions for the deposition of cadmium sulfide and cadmium telluride films in a quasi-closed space on polyimide substrates and to test the possibility of high-efficiency flexible photoelectric converters obtaining by QCA method.

MATERIALS AND METHODS

The development of equipment for the deposition of sulphide and cadmium telluride films in a quasi-closed area: In order to deposit the films of sulphide and cadmium telluride, two graphite chambers should be included in the equipment, each chamber consists of a condensation zone in which the substrate is located and an evaporator area. The equipment also includes a multi-channel electronic system for monitoring and maintaining the required condensation temperature with temperature measurement directly on the front surface of a substrate; the system of substrate mechanical displacement from one chamber of a quasi-closed area to another for successive deposition of CDs and CdTe layers.

In order to implement the conditions close to the thermodynamically equilibrium ones, the mass flow of cadmium sulfide and cadmium telluride vapor from the vapor phase must be completely compensated by the mass flow of materials from the source of element vapor cloud due to the excess of the evaporation surface area in a source relative to a substrate area. At that the degree of a substrate adherence to a source should minimize the leakages to the external volume which should not exceed 5%.

Based on these requirements, the design of Quasi-Closed Volume (QCV) chambers was developed consisting of the following structural elements: base, neck, preparation zone, evaporator, ring, screen, screen cover, rack and heaters. A schematic view of QCV chamber is shown on Fig. 1 and 2.

In order to use standard industrial vacuum devices during the design of tooling, it was stipulated that two graphite QCV chambers are installed on a standard plate of the vacuum station UVN-71 at the first and the third position. The second position is used to perform the pre-heating operation of a substrate. The holder of the substrate with the heater was structurally integrated into a single unit and placed on a carousel. The carousel

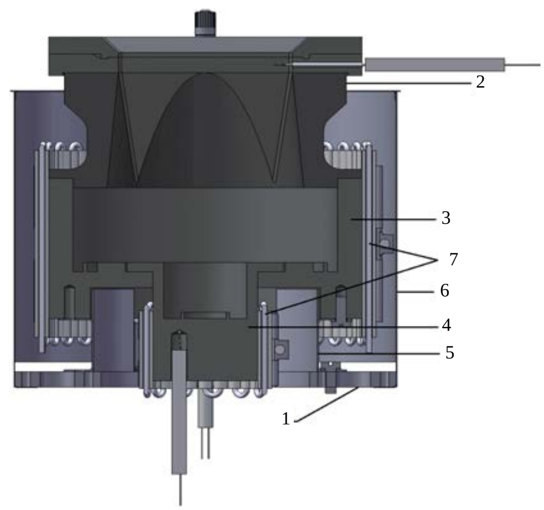

Fig. 1: Schematic view of the developed QCV chamber; 1-base, 2-neck, 3-preparation area, 4-evaporator, 5-ring, 6-screen, 7-heaters

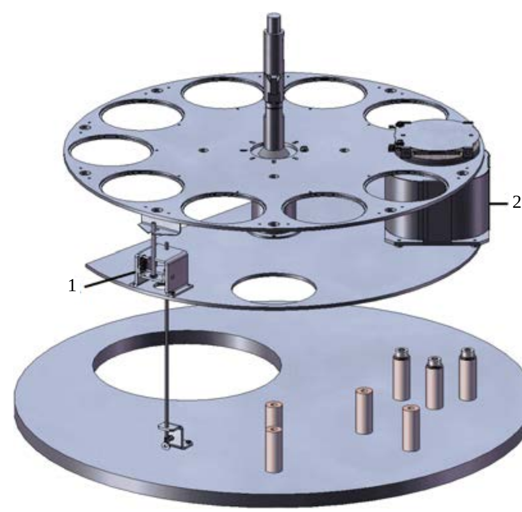

Fig. 2: Schematic view of the carousel with the installed QCV chamber 2 and the stopper 1

rotation assembly has been modified to allow the holder to move with the heater in the vertical direction. For this, the carousel was attached to the running nut which is located on a lead screw. The lead screw is installed in the regular assembly of the bearing for UVN-71 carousel rotation unit. The rotation of the rotary screw is transferred from a regular input of the carousel rotation, located in the upper part of the UVN-71 cover through the coupling to the rotation nut fixed to the shaft. In order to prevent the carousel rotation a latch is used in this case, operated from the electromagnet of the damper drive.

(a) (b) (c)

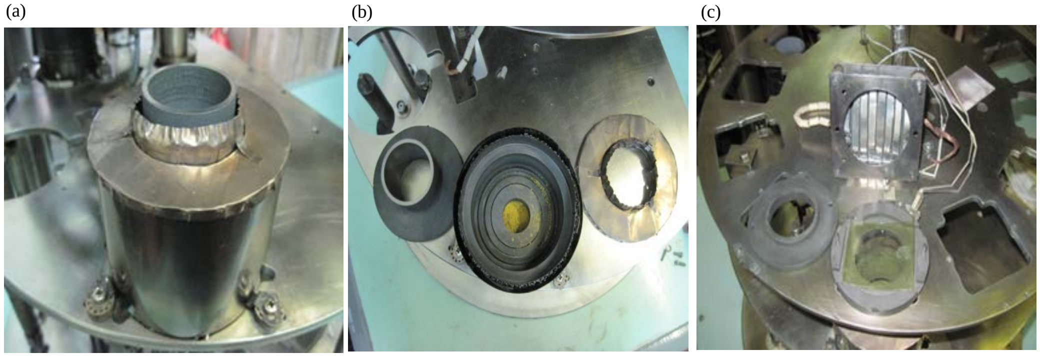

Fig. 3: Technological equipment for sulphide and cadmium telluride heterosystem application in a quasi-closed area

Thus, the rotation of the carousel rotating input shaft clockwise/counterclockwise causes the travel nut movement along a drive shaft and hence to the carousel movement up and down. The carousel rotation (a sample movement between the positions) is possible with the lock released in the uppermost position of the carousel, when the running nut rests against the lower end of the rotation nut. A schematic view of the carousel providing the fulfillment of these requirements is shown on Fig. 2. Evaporative compartments made from the graphite of two identical quasi-closed area precipitation chambers (Fig. 3a) for the deposition of the basic sulphide and cadmium telluride heterosystem in a single technological cycle were filled preliminary with sulphide (Fig. 3b) and cadmium telluride powders. In order to place the polyimide film in a QCV chamber a graphite substrate was manufactured with a metal holder was made which was covered with a strip heater (Fig. 3c).

RESULTS AND DISCUSSION

Experimental determination of the critical deposition temperature for telluride and cadmium sulfide films in a quasi-closed area: An important characteristic of film growing process in QCV is the initial condensation temperature T_{cr} the temperature of a substrate at which the critical supersaturation of vapor is reached and it becomes possible to generate condensate particles on a foreign substrate. The difference between the selected substrate temperature T_i and T_{cr} serves as one of the criteria to deviate from the conditions of the condensate growth initial stage from the equilibrium ones. At that the peculiarity of film deposition on a polyimide substrate is that the temperature of the substrate should not exceed the temperature of its thermal stability which makes 450°C.

Therefore, an experimental determination of T_{cr} was carried out at the condensation of cadmium telluride vapor on glass substrates in the temperature range T_i = 425-560°C. At that the following procedure was applied. A substrate was installed in a manufactured graphite chamber which overlapped densely the entire cross section of the chamber. CdTe hanging of (concentration of the main component >99.99%) brand in the form of a fine batch was placed on the bottom of the chamber, covering its entire area. In order to control the substrate temperature, the chromel-aluminum thermocouple with the diameter of 0.15 mm was placed on the front side of the substrate at the distance of 10-11 mm from the outer edge of the condensation zone. The heating of the evaporator and the substrate was carried out by two independent heaters under the control of an automatic system. In order to heat the substrate they used the radiation heater, the design of which provided the creation of a radial temperature gradient on the substrate from the center to the edge.

The power of chamber zone heaters was chosen in such a way that the rate of the substrate heating exceeded the heating rate of other zones that is the condition $T_i>T_{cr}$ was realized for the entire surface of the substrate. After the achievement of the selected T_i value, the substrate temperature was reduced to a certain value that is the condition $T_i<T_{cr}$ was realized. This temperature regime was maintained for 5-10 min after which the evaporator heater was turned off. The substrate heater was switched off only when the evaporator temperature was 30°C less than the substrate temperature. Such a three-stage operation allows to avoid the condensation of vapor on the substrate in nonstationary heating modes. Thus, condensate was developed on the substrate in the form of a ring whose outer iameter is limited by the wall of the chamber condensation zone. The inner boundary of the ring corresponds to the region of the substrate whose temperature is = T_{cr}. In a series of experiments with a fixed value of T_i, the temperature regime on the substrate was chosen in such a way that the internal boundary of the

Table 1: Experimental results on the determination of the initial critical condensation temperature

T_i (°C)	T_{cr} (°C)	T_i-T_{cr} (°C)
541	443	98
503	402	101
461	357	103
455	351	104
425	319	106

condensate only reached the place of the thermocouple installation. In this case, the thermocouple readings corresponded to the value T_{cr} at a given evaporation temperature. At the same time, the absence of condensation was controlled on the chamber walls near the substrate. The results of the experiment are shown in Table 1. Data analysis shows that when T_i is decreased from 541-425°C, the decrease of T_{cr} from 443-319°C is observed with an insignificant increase in the difference (T_i-T_{cr}) from 98-106°C.

A similar approach was applied during the determination of the critical deposition temperatures for cadmium sulfide films. It was found that when evaporator temperatures are below 548°C, the development of condensate in the form of a ring is not observed. From our point of view, this is conditioned by the lower pressure of saturated cadmium sulphide vapors as compared to cadmium telluride at a fixed evaporator temperature (Medvedev, 1979). It was found that when evaporator temperature makes 548°C, the critical deposition temperature of cadmium sulphide makes 440°C. When the temperature of cadmium sulphide evaporator increases, the critical temperature exceeds the stability temperature of the polyimide.

It was determined during the research that satisfactory stability and the reproducibility of cadmium telluride film properties was achieved under the conditions when the substrate temperature was kept at 3-4°C below T_{cr} and at 5-6°C below for cadmium sulfide. In this case, the thicknesses of films obtained under the same technological conditions differed not more than by 7%. From our point of view, the cause of such a spread is the uncontrollability of the transient processes when the chamber is heated.

Sulfide and cadmium telluride film crystal structure obtaining and study: The application of cadmium sulfide films was carried out on flexible substrates which were represented by polyimide films on which an ITO layer was applied with a nanosized ZnO interlayer by magnetron deposition method. When the holder with the substrate was installed on the carousel, the working volume was pumped out to the pressure of no >2×10^{-5} mmHg. After this, the cadmium sulphide evaporation chamber and the substrate holder were preheated to degasify their surfaces. At that both chambers were open and the sample holder was located in the preheating position. In order to prevent a thermal shock, the heating rate of the elements does not exceed 40°C/min. The degassing temperature of all elements in the range of 300-340°C, the holding time at this temperature is not <4 min. The quality criterion for degassing is the restoration of vacuum degree in the working volume of the device up to the level no worse than 2×10^{-5} mmHg. After degassing, the assembly of quasi-closed area chamber was performed to apply CdS layer. For this purpose, the holder with the heater was set to the position above the chamber and lowered to the neck by rotating the assembly drive for the carousel movement. Then the zones of QCV chamber were heated and the temperatures of steam preparation zone and the evaporator were stabilized at 548°C and the substrate temperature was 445°C. This mode of QCV chamber zone heating prevents an uncontrolled condensation of steam on the substrate during this operation. The accuracy of temperature maintaining was equal ±1°C when the set values reached. The application of CdS layer to the substrate continues for 5 min. For this purpose, the temperature of the substrate is reduced to 434°C at the specified temperature of steam preparation zone and the evaporator temperature. The beginning of the layer application is considered to be the time when the substrate temperature reaches a predetermined value. When the application process is over, the power supply of the evaporator heaters and the chamber is turned off and the chamber is cooled and the substrate temperature is increased to 445°C and kept constant until the temperature difference of the chamber zones does not exceed 10°C. After that the substrate and the chamber are cooled to the temperature of 400°C.

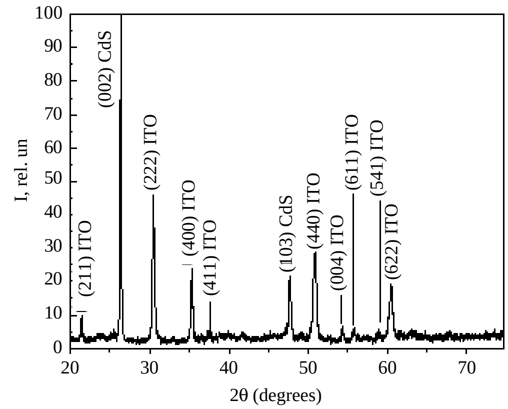

Fig. 4: X-ray diffractogram of cadmium sulfide films developed on a flexible substrate with ITO film layer and a nanosized ZnO interlayer

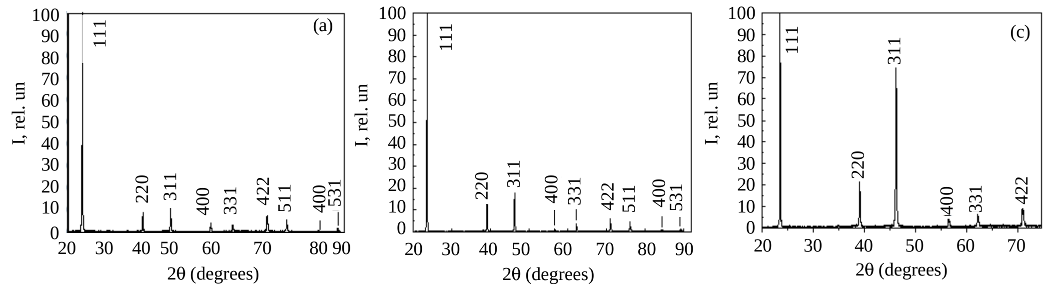

Fig. 5: Diffractograms of cadmium telluride films obtained at different substrate temperatures; a) T_s = 353°C; b) T_s = 398°C; c) T_s = 439°C.

The crystal structure of the obtained cadmium sulfide films was studied. The thickness of these films was 0.3 μm. Such thickness of cadmium sulfide layers is used during the design of high-efficient FPC based on cadmium telluride. The analysis of X-ray diffractograms for cadmium sulfide films deposited on polyimide substrates with an ITO sublayer (Fig. 4) showed that they have the crystal structure of a stable hexagonal cubic modification CdS. The presence of multiple reflections (002) and (004) suggests that they are oriented mainly in [002] direction.

When the technology of CdS layer application was developed, the application of cadmium telluride films was carried out in a single technological process with the application of cadmium sulfide films. After the application of CdS layer and the cooling of the substrate to 400°C, it was lifted and moved to the second QCV chamber where the sequence of operations eas performed similar to the sequence of CdS layer application. The application time of CdTe layer was 25 min. For three evaporator temperatures of 461°C, 503°C, 541°C and at deposition temperatures that were 4°C lower than the corresponding critical temperatures (Table 1) and made 353, 398 and 439°C respectively the cadmium telluride films with the thickness of 4 μm were obtained on the surface of ITO/ZnO/CdS heterosystems.

The studies of cadmium telluride film crystal structure were carried out using X-ray diffractometric analysis. The phase analysis showed that the films of of cadmium telluride with a stable cubic modification are developed within the indicated regimes as evidenced by the presence of reflections from the (111) (400) (511) (220) (311) and (422) planes (Fig. 5). Since the thickness of CdTe layers was 4 μm, the diffraction peaks from CdS and ITO layers were not identified at the background level. The analytical processing of X-ray diffractograms made it possible to determine the half-width of the cadmium telluride diffraction maximum (111) which is an integral indicator of the structural perfection for film layers. It was found that the monotonous growth of the half-width of the diffraction maximum (111) was observed from B_{111} = 0.13 at T_s = 353°C to B_{111} = 0.09 at T = 439°C as the substrate temperature increased. Thus, the most structurally perfect cadmium telluride films were obtained at the substrate temperature of 439°C.

Reception and research of flexible photoelectric converters based on cadmium sulphide and telluride: The obtained CdS/CdTe heterosystems were approved in the composition of flexible photoelectric converters. To do this they were subjected to “chloride” treatment during which the layers of cadmium chloride were applied on the surface of cadmium telluride without the substrate heating. Then the systems were annealed in the air at 430°C for 25 min (Khrypunov, 2005). After the etching in bromine solution and methanol a back contact was developed on the base layer surface by a copper film application with the thickness of 11 nm and then a gold film with the thickness of 50 nm was applied (Khripunov, 2006). After that the obtained FPC was annealed in the air at the temperature of 250°C for 20 min.

In order to determine the output parameters we studied the VAC of FPC with a luminous flux of 100 mW/cm^2 (Fig. 6). After the analytical processing of VAC, the output parameters of FEP were determined which are presented in Table 2.

The analysis of results shows that with the deposition temperature increase of cadmium telluride films from 353-439°C, the increase of FEP efficiency is observed from 10.5-12.2% on the basis of CDs/CdTe which is caused by a simultaneous increase of the short-circuit current density J_{cd} from 21.2-21.8 mA/cm^2, the no-load voltage U_{nl} from 788-820 mV and VAC FF filling factor from 0.625-0.680.

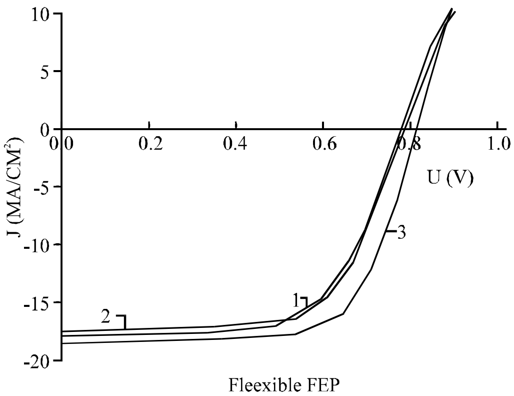

Fig. 6: VAC of flexible FEP based on cadmium sulphide and telluride (1-T_s = 353°C, 2-T_s = 398°C, 3-T_s = 439°C)

Table 2: Output parameters of flexible photoelectric converters based on cadmium sulphide and telluride

	Deposition temperature (°C)		
Output parameters	353	398	439
J_{cd}, mA/cm^2	21.2	20.8	21.9
U_{nl}, mV	788	784	820
FF (rel.un)	0.625	0.653	0.680
η (%)	10.5	10.7	12.2

CONCLUSION

They developed and tested the technological equipment for a vacuum installation in order to obtain cadmium sulfide and telluride films on flexible substrates by the condensation from a quasi-closed area. This equipment makes it possible to deposit cadmium sulfide and telluride layers in a single technological cycle sequentially without the vacuum disturbance on polyimide substrates under the conditions close to thermodynamically equilibrium ones.

The experimental studies of film condensation critical temperature in the quasi-closed area of cadmium telluride made it possible to determine the evaporator temperature depending on the required substrate temperature, at which the condensation of films is performed under the conditions close to thermodynamically equilibrium ones.

They obtained the layers of cadmium sulfide with the thickness no more than 0.3 µm in a quasiclosed area at the deposition temperature below 450°C on polyimide films with an ITO layer of a stable hexagonal modification and the layers of cadmium telluride of a stable cubic modification on their surface with the thickness of 4 µm. The degree of cadmium telluride layer structural perfection increased with the deposition temperature increase up to 439°C. The use of the obtained heterosystem in the composition of flexible photoelectric converters shows that the efficiency increases to 12.2% with the increase of cadmium telluride layer deposition temperature up to 439°C.

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