PHYSICAL SCIENCES

OBTAINING CdTe FILM BY CHEMICAL METHODMOLECULAR BEAM DEPOSITION IN A HYDROGEN FLOW AND ITS COMPREHENSIVE STUDIES

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Abstract
The CMPO method for growing CdTe films with different compositions. Isolated Cd and Te sources with a purity of 99.9% and 99.999%, respectively, were used. The films were deposited on glass and a molybdenum substrate and kept at a temperature of 500 ^{0}C. The samples were grown at atmospheric pressure in a hydrogen or nitrogen flow. The thickness of the obtained films varied from 0.5 to 1.5 μm. The effects of heat treatment on the electrophysical properties of CdTe films obtained by the CMPO method were investigated and the physical properties were comprehensively investigated . To study the physical properties of CdTe films, the authors used a comprehensive research method. The conductivity type of the obtained films, electrical conductivity and its temperature dependence, the Hall Effect and measurement of the I–V characteristics of the heterostructure were determined. Optical metallography, X-ray diffraction and atomic force microscopy were also used.

Keywords: Chemical molecular beam deposition, films, optical metallography method, X-ray diffraction, atomic force microscope.

Introduction . As is known, thin-film solar cells based on CdTe are the main contenders for global commercialization in the field of semiconductor photovoltaics. Recently, **much** attention has been paid to the research and development of thin-film solar cells based on CdTe. This is due to the direct band gap and high absorption coefficient of the semiconductor, in which the incident radiation is completely absorbed in the micron thickness. Therefore, significant progress has been achieved in this area in the field of research of CdTe-based materials, in the production of photovoltaic devices and the development of technology for creating semiconductor solar cells.

Currently, the world achievement of the efficiency of thin-film CdTe solar cells is 16.5% using a modified device structure [1-3]. Most of the methods have been used to fabricate CdTe layers, such as sublimation in a closed volume, electrodeposition, magnetron sputtering, chemical vapor deposition, metal-organic chemical vapor deposition. It should be noted that the efficiency of 16.5% was obtained by the sublimation method in a closed volume. However, it has been shown that the efficiency of thin-film CdS-CdTe solar cells can be achieved up to 20-25%. To achieve such high efficiencies, it is necessary to have a detailed understanding of the basic properties of the materials and the processes involved in the fabrication of the structures. One of the key points in the fabrication of the structures is the deposition of CdTe films with a controlled composition, since a thin layer of tellurium-rich material on the surface is necessary to form a high-quality ohmic contact.

Production of CdTe films. We have previously reported on a new low-cost method of chemical molecular beam deposition for the production of films of ^{II} – ^{VI} compounds and binary compounds at atmospheric pressure in a gas flow [2]. X-ray structural analysis of CdTe films shows that grain orientation predominates in these structures [3]. A linear dependence between the ratio of the molecular beam intensity in the vapor phase and the film composition has also been shown [4,8,9]. This monograph presents the results of studies of the properties of CdTe, CdS and Mo/ CdTe / CdS heterostructures grown by CMBD methods both enriched with cadmium and with a close stoichiometric composition.

CdTe films of different composition obtained at a low condensation temperature. Currently, the most efficient thin-film solar cells are created on the basis of CdTe, Cu (In, Ga) Se $_2$ semiconductor materials , the record efficiency values of which are 16-17% and 19-20%, respectively [1,5,4]. Despite the significant progress achieved in this area, none of the existing more than 10 technologies allows controlling the composition of CdTe films, since their physical properties are mainly determined by their own point defects. It should

be noted that when choosing a technology for the manufacture of thin-film solar cells for terrestrial use , in addition to the physical and technological capabilities of these processes, special attention should be paid to their cost-effectiveness, the degree of reproducibility of the manufactured films, the possibility of full automation of the processes, as well as the possibility of depositing films on large areas for use in mass production.

Previously, we reported on the production of CdTe films of various compositions at a deposition temperature of 600 ^{0}C by means of chemical molecular beam deposition (CMBD) in a hydrogen flow, and their complex physical properties were also investigated. In this paper, the production of CdTe films of various compositions at a lower temperature of 500 ^{0}C is discussed and their electro physical properties are investigated [2].

To study the physical properties of CdTe films, the authors used a complex research method. The complex study of the films consisted of studying the type of conductivity, electrical conductivity and its temperature dependence, the Hall Effect, and measuring the current-voltage characteristics of the heterostructure. The methods of optical metallography, X-ray diffraction, and atomic force microscopy were also used.

To perform electrical measurements, ohmic contacts were applied to freshly deposited films by vacuum deposition. Silver and silver paste were used as ohmic contacts for hole-type films, and indium or indium-gallium alloy for electron-type films. The sign of the thermo-EMF determined the conductivity type of the samples. Using a V7-30 electrometer with an input resistance of more than 10 ^{14} Ohm to indicate the sign of the thermo-EMF made it possible to determine the conductivity type of high-resistance samples with a specific resistance of more than 10 ^{8} Ohm · cm.

The ohmic properties of the contacts were checked by measuring the current-voltage characteristics and studying the potential along the sample. The samples whose current-voltage characteristics did not show rectification in the range of measured voltages and temperatures, and whose potential distribution along the sample was linear, were considered high quality for further studies. The geometric dimensions of the samples and the distance between the probes were measured using a microscope. The specific resistance (ρ) and the Hall constant (R_x) in the films were measured using the Van der Pauw method. Measurements ρat low temperatures of 80-300 K were carried out in a specially designed vacuum cryostat using a ceramic terminal with an insulation resistance of more than 10 ^{13}-10 ^{14} Ohm, which made it possible to measure ρin samples with a specific resistance of more than 10 ^{8} Ohm·cm. The cryostat is distinguished by its reliability, simplicity and economy of operation (the consumption of liquid nitrogen for measurements in ρone sample in the range of 80-300 K was 0.5 l).

Film thicknesses (up to 2-3 μm) were determined using an MII-4 microinterferometer and precision microweighing using a VLR-20 balance. A MIM-7 metallographic microscope was used to measure the thickness of thicker films and the grain size, as well as to study the surface morphology. The microstructure of the films was studied using an atomic force microscope (AFM) JEOL 6400. Energy dispersive spectroscopy based on a JEOL 6400 was used to determine the film composition. X-ray structural analysis was performed using a Philips APD 3720 device.

To study the electrophysical properties of CdTe films, the specific resistance, Hall constant (R_x) and temperature dependence were measured using the above-mentioned Vander Pauw method.

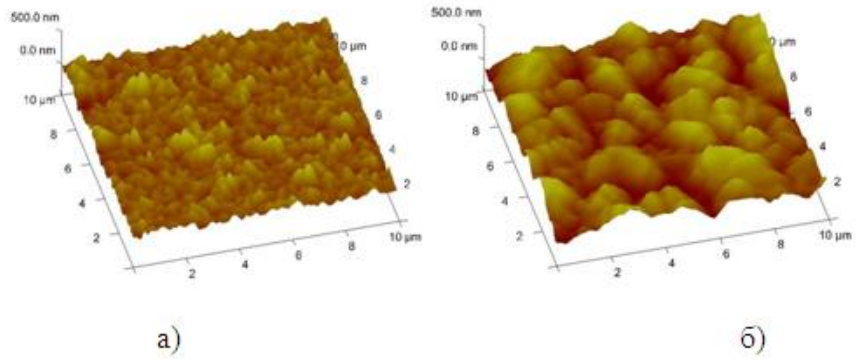
Samples with the composition Cd/Te = 0.5 had p-type conductivity, and with the composition Cd/Te = 1.16 had n-type conductivity, due to the cadmium vacancy V_{Cd}^{-} and the tellurium vacancy V_{Te}^{++}, respectively. While the stoichiometric composition of CdTe films has the highest specific resistanceρ ~10 ^{9} Ohm ·cm.

Heat treatment of the $CdCl_{2\ solution}$ significantly reduced the resistivity of the stoichiometric CdTe film from 10 ^{9} O m.cm to 10 ^{6} O m.cm. While the resistivity of the samples enriched in Cd and Te is small, the changes and remained ~10 ^{6} Ohm.S. These results suggest that heat treatment of $CdCl_2$ does not always result in grain enlargement , especially for coarse-grained films , but it does affect the intrinsic point defects in cadmium telluride.

CdTe films can be considered as a compensating material containing an acceptor level $EV_{+0.15}$ eV and a donor level EC - 0.48 eV. The physical properties, especially the resistivity of CdTe films are controlled depending on the activity of these levels. The level EC - 0.48 eV is a tellurium vacancy, predominant for Cd-enriched films and the samples had n-type conductivity. The level $EV_{+0.15}$ eV is a cadmium vacancy, predominant for Te-enriched films and the samples had p-type conductivity. We observed a significant decrease in the resistivity of stoichiometric CdTe films upon treatment with $CdCl_2$. This occurs due to the formation of a new level $EV_{+0.15}$ eV, which is associated with VTe^{++} tellurium vacancy and oxygen .

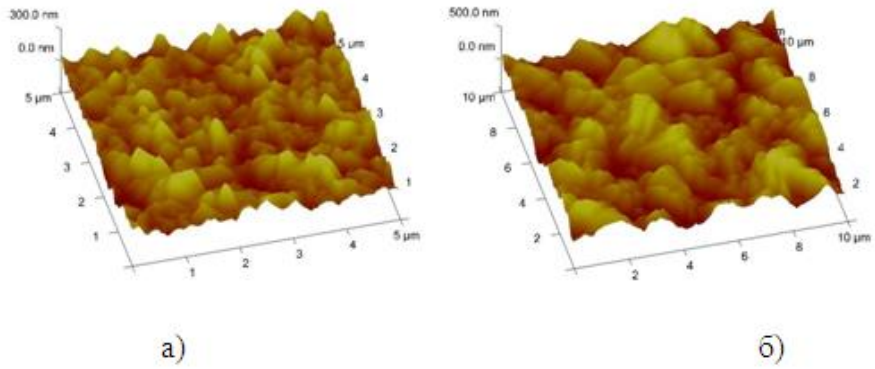
However, the reduction in resistivity of CdTe films by treatment with CdCl2 solution $_{is}$ limited to approximately ~106 $^{\Omega}$ cm. The efficiency improvement of CdS-CdTe thin film solar cells requires much less resistivity. Resistivity of CdTe films up to 104 $^{-}$ 106 $^{\Omega}$ cm can be achieved by deviating the film composition from stoichiometry during the growth process by CMBO methods. Therefore, there is no need for heat treatment with CdCl2 solution $_{for}$ CdTe films grown by CMBO method. This new and low-cost CMBO method can be successfully used to fabricate CdS-CdTe thin film solar cells with high productivity.

The morphological properties of CdTe films of different compositions obtained by the CMPO method were investigated. Morphological studies were carried out using an atomic force microscope (AFM), by obtaining a 3D image .



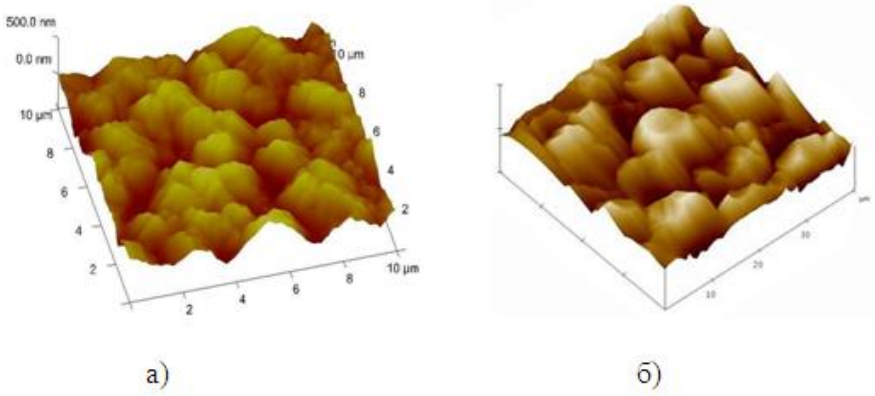
а) б)

1) Sedimentation rate: a) 1.5Å/sec b) 0.9Å/sec



а) б)

2) Film thickness a) 0.3 µm b) 0.5 µm



а) б)

3) Substrate temperature. a) 500 ^{0}C, b) 600 ^{0}C.
Fig.1.3 D AFM images of CdTe film obtained by the CMPO method

Figure 1 is a 3D image of the AS M for CdTe samples obtained at a substrate temperature of 500 ^{0}C. As can be seen from the presented 3D image in Fig. 1, with an increase in the deposition rate at a constant substrate temperature, the grain sizes of the CdTe films decrease. and leads to deterioration of the crystalline structures of the samples. While with an increase in the condensation temperature and film thickness At a constant sedimentation rate, the grain sizes increase and the morphological properties of the samples improve.

The dependence of the grain size and crystallinity of the films on the deposition rate (condensation temperature) can be explained by the fact that at high molecular beam intensity (MBI), i.e. density, the condensing atoms on the substrate surface do not have time to migrate at the required speed over the surface. Since each condensing layer of atoms is under the pressure of the next incoming layer, i.e. each incoming layer of molecules limits the mobility of the molecules of the previous layer. This prevents the formation of crystals and leads to the formation of a fine- grained structure. Therefore, to obtain high-quality coarse-grained films, it is necessary to ensure the following condition: the density of the incident flows must be equal to the density of the condensing flow $R \approx R_{to}$ This also causes a decrease in the minimum condensation temperature of crystalline films at low IMF. Since in this case the probability of collision of particles that hit the substrate decreases, and, consequently, their surface mobility increases. Therefore, the atoms have time to complete the

construction of the crystal lattice. As a result, crystalline films are formed. These processes are described in detail in our article [6].

Based on the analysis of the films by AFM, obtained 3D images (Fig. 1a, b), it was revealed that the films obtained at a substrate temperature of 500 ^{0}C had a well-oriented polycrystalline structure, the desired grain size of 2-3 μm, and were more densely packed than the films grown at a substrate temperature of 600 ^{0}C. This makes it possible to grow CdTe films with deposition rates of 0.9 ~ 1.5 A/sec at a substrate temperature of 5000 C , which are suitable for the manufacture of photovoltaic devices.

The deposition of CdTe was successful, but our goal is to use it in multilayer solar cells with adjustable band gap. It is reported in the literature that multilayer solar cells provide higher efficiency due to the higher internal electric field (E_i) $_{generated}$ inside the device. The CdTe film grown in this work is rich in Te as shown by Raman, XPS and EDX measurements. Further work is needed to improve the layer and obtain stoichiometric CdTe, which is necessary for good devices.

CdTe was deposited on glass/ FTO / ED - CdS and molybdenum substrates using a low-cost gas transport method under hydrogen flow. PEC measurements confirmed that the electrodeposited layers produce CdTe n- , i- and p -type simply by changing the deposition voltage. The XRD results for both as-deposited and heat-treated materials confirm a cubic structure with a preferred (111) orientation. Near the stoichiometric growth region, only the (111) peak is dominant, indicating better crystallinity due to the presence of a single CdTe phase. Far from the stoichiometric region, the crystallinity is poor due to the presence of two phases: Te or Cd , in addition to the CdTe phase .

SEM studies show that the deposited layers had small holes between the crystallites. Their proportion depends on how far from the stoichiometric position. 3D-AFM images show that the CdTe has a highly ordered and closely packed column perpendicular to the substrate. From the Raman spectroscopy data, two peaks attributed to CdTe and one peak of Te were identified, indicating the presence of excess Te and TeO compound of the $_{2-}$ i interface layer in the CdS / CdTe heterostructure . The XPS work shows that the deposited CdTe has a spectrum similar to that of pure cleaved CdTe , except for the additional presence of C and O peaks , which may be due to surface contamination.

It was found that the thickness of CdTe affects the performance of the solar cell. For comparison, six samples grown with different thicknesses were characterized by different methods. IV measurements for the finished glass/ FTO / ED - CdS / CdTe / Au devices yield a maximum efficiency of 7.60% at V_{oc} ~ 660 mV, J_{sc} ~24 mA cm $^{-2}$ and FF ~0.48 were achieved in 5 h of CdTe growth . The efficiency decreases as the thickness increases or decreases. Based on the log I and V , rectification factor (RF) ~10 ^{3,} n value . ~1.88 and φ_B were achieved ~1.20 eV . Capacitance-voltage measurement gives V_d ~1.35 eV and doping concentration (N_D) ~2.0 × 10 ^{17} cm $^{-3}$.

It is shown that intergranular barriers are formed due to accumulation of localized charges at grain boundaries. It is established that the current through intergranular boundaries in large-block CdTe polycrystals obeys the laws of thermionic emission.

Conclusions. The barrier height at intergranular boundaries in large-block p - CdTe polycrystalline films has been experimentally determined . It has been shown that exposure to white light significantly increases the mobility of the majority charge carriers, which can facilitate the production of low-resistance substrates from CdTe polycrystals . The conducted photoconductivity studies show that the electron states of extended defects, exciting electric fields and elastic stress fields around themselves, are most likely determined by the atomic structure of extended defects, in particular, the presence of dangling bonds. For final confirmation (or refutation) of this opinion, it will be necessary to use more complex research methods in the future , primarily local-structural ones. It has been established that the value of $\mu_p \tau_p$ for the nCdS / pCdTe heterostructure increases with increasing temperature . For example, the value $\mu_{of\,p}\tau \approx 1.43 \cdot 10^{-7}$ cm ^{2} /V at T = 293 K, and at T = 353 K – $\mu_p \tau_p \approx 3.9 \cdot 10^{-7}$ cm ^{2} /V.

The authors succeeded in obtaining CdTe films of various compositions at reduced substrate temperatures using the CMPO method . It was found that after heat treatment in a $CdCl_{2\ solution}$, the resistivity of a stoichiometric CdTe film decreased significantly from 10 ^{9} Ohm.cm to 10 ^{6} Ohm.cm. While the resistivity of samples enriched with Cd and Te is small, the and remained ~10 ^{6} Ohm.cm. It is shown that for CdTe films obtained by chemical molecular beam deposition there is no need for such treatment. Based on atomic force microscopy images , it was found that the films obtained at a substrate temperature of 500 ^{0}C had a well-oriented polycrystalline structure, where the grain size was 2-3 μm, and more densely packed than the films grown at a substrate temperature of 600 ^{0}C. This makes it possible to grow CdTe films with a deposition rate of 0.9 ~ 1.5 A/sec at a substrate temperature of 5000 C , which are suitable for the manufacture of photovoltaic devices.

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