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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

ELEKTROPHYSICAL AND PHOTOELEKTRICAL PROPERTIES OF SEMICONDUCTOR STRUCTURES ON BASIS OF CdS GROWN (CREATED) IN NANOPOROUS ALUMINUM OXIDE

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GENERAL DESCRIPTION OF THE WORK

Relevance of the research topic. At present day, environmental problems in the countries of the world are solved mainly by the use of renewable energy sources and mainly solar and wind energy. This is one of the affecting factors to the development of energy, economy, industry, and other sectors. Solar photovoltaic devices (that is directly converting solar energy into electrical energy, for example, solar cells and batteries) and the devices that operate on photovoltaic principles have a special place in alternative and renewable energy sources. Solar cells and batteries that are not polluted environment is widely used both of power supplies of spacecraft, homes and villas, power supply of mobile communications transmitters, lighting of roads, protection of soldiers life on the desert and waste areas, protection of oil and gas tube surfaces, to charging large batteries and mobile phones, etc.

Synthesis of high-efficiency semiconductor materials in the visible light region and their electrophysical, optical and photoelectric properties for converting solar energy into electrical and chemical energy is one of the actual problems. Different methods have been used to solve this problem. For example electrochemical deposition, vacuum magnetron deposition, thermal evaporation, and close space sublimation. Among these methods, the electrochemical deposition method has great potential to obtain thin and nanostructured layers of semiconductors. First of all, it should be noted that the electrochemical deposition method can be easily manipulate Synthes prosses by changing the composition of the electrolyte and electrolysis conditions to obtain semiconductors with the essential properties. This also provides superiority of electrochemical deposition method from other methods.

The increasingly expanding use of semiconductor layers and nanostructures in solar power engineering has to get actual under the condition to keep the high level of optical, electrical, and photoelectric properties preparing with simple and inexpensive technology problems. In this case, as optical transparent and conducting layers In_2O_3:Sn, as window layer CdS, as absorbent layer CdTe thin layers and nanostructures getting with physical and electrochemically methods, to research their properties also today it is not losing their actualities in high-efficiency semiconductors in the visible region of the solar spectrum used in modern solar cell converters. To optimize and improve the parameters of such structures and solar cells based on them and their technology, it is important to study their physical properties. In the J.A. Guliyev dissertation work on the optical transparent, conductive layers of In_2O_3:Sn and electrical connectivity, optical transmittance spectrum and crystal structure properties mechanism of dependence from their manufacturing methods of CdS such as window thin layers, nanoscale pillars based on CdS built-in inside the nanoporous Al_2O_3 matrix, the result of expanding to the short wavelength of optical transmittance spectrum, Raman scattering, and photoluminescence process, photocurrent and photo effect creating mechanism in the heterostructure formed between nanowire CdS and thin-film CdTe were identified. The results of these studies are important and actual for increasing the efficiency and productivity of solar cells, sensors and other photoelectron devices, based on these materials. From this point of view, the topic of the dissertation is actual and the results of the research are of great scientific and practical importance.

Purpose and objectives of the study: Development of physical bases for obtaining glass/In_2O_3:Sn/Al_2O_3/CdS/CdTe based nanostructures, to determine the mechanisms of optical, electrophysical and photoelectric phenomena occurring in them and the development of practical recommendations for the creation of solar cells based on these structures.

The following tasks were set to achieve this goal:

- Development of In_2O_3:Sn, CdS and nanoporous Al_2O_3 thin films extraction technologies;
- The development of preparation of CdTe thin films by electrochemical deposition, and close space sublimation methods;

- Research of electrophysical, optical, structural, photoelectrical, etc. properties of individually In_2O_3:Sn, Al_2O_3, CdS, and CdTe thin films and (glass/In_2O_3:Sn/CdS, glass/In_2O_3:Sn/Al_2O_3/CdS/CdTe and etc.) structures created based on these;
- Development of practical recommendations for the creation of solar cells based on nanostructured glass/In_2O_3:Sn/Al_2O_3/CdS/CdTe structures.

Research objects and methods:

An electrolyte containing 0.125M $CdSO_4$, 0.25M Na_2SO_3, 0.35M H_2SO_4, 0.007M Trilon-B ($C_{10}H_{14}O_8N_2$:H_2O) and dissolved in anhydrous Ethylene-glycol at a temperature of T=130^{0}C containing 0.2M $CdCl_2$, 0.02M S_8, və 0.1M NH_4Cl solutions were selected as a research objects for performing of dissertation. The deposition process in the first solution is carried out by the IVIUMSTAT electrochemical potentiostat analyzer, in the second solution, it was carried out in a two-electrode cell created in the laboratory. X-ray analysis of the layers using CuKα (λ = 1.54060 Ǻ) diffractometers of Rigaku Miniflex-500 and X-Ray diffractometer D2 Phaser (Bruker, Germany), The morphological analysis of the surface was characterized by Smart SPM 1000 AIST NT atomic force microscope, Carl Zeiss Sigma scanning electron microscope (SEM), and energy dispersion spectra (X-ray EDS) by Oxford Instruments SEM. Optical transmission and absorption spectra of samples measured on a Specord 250+ UV / VIS Spectrophotometer, Raman and photoluminescence spectra measured using a spectroscope of Nd: YAG (λ = 532nm) Tokyo instruments Nanofinder 30-NM01 (Tokyo Instruments, Inc.) device. The characteristics of the solar cells were measured using the Solar cell I-V Tester Model IV16K (PV Mesurements Inc, USA) solar simulator. The thickness of the layers was measured on an MII-4 interference microscope and a Rotating Compensatory Ellipsometer M2000-DI (J.A. Woollam Co.Inc. the USA) ellipsometry device. The resistivity of the samples, mobility and conductivity type was measured by the Van-Der-Pau method using a standard 4-probe device and a thermal probe.

Main provisions for the defense:

- The electrical and optical properties of In_2O_3:Sn in transparent conductive thin layers obtained by vacuum magnetron sputtering in a medium of oxygen/argon gas mixture of different ratios (0, 5 and 10%) and annealed in the temperature range of 200–500°C were studied and mechanisms of transportation and optical phenomena have been identified.
- It was found that the high electrical conductivity and optical transmission in the thin layers of In_2O_3:Sn were obtained as a result of thermal treatment in air at a temperature of 500ºC at 0 and 5% oxygen/argon ratios, respectively. In_2O_3:Sn observed in thin layers, the reason for the decrease in the conductivity of these layers with increasing oxygen content in the O/Ar mixture (3.5×10^2 Ω/□ at 500ºC). Explained by the decrease in the concentration and mobility of carriers as a result of the formation of acceptor-type Sn vacancies in In_2O_3:Sn.
- A thin layer of aluminum deposited on glass substrates coated with a thin layer of In_2O_3:Sn can be changed by anodic oxidation at anode diameter of 5–100 nm and thickness in the range of 300 nm ÷ 1 µm. developed, the mechanism of the oxidation process was determined, their surface morphology, structure, optical properties (transmission and Raman shift spectrum) and element compositions were characterized by different methods.
- The electrolyte composition and electrolysis conditions required for the electrochemical extraction of CdS layers were determined, as well as the potential area for joint deposition. The precipitation potential area of cadmium ions in the selected electrolyte solutions was determined, along with the precipitation potential area of sulfur ions, their deep reduction potential area up to sulfide ions was determined.
- The technology of electrochemical deposition of CdS layers obtained on the Glass/In_2O_3:Sn/AAO structure has been

developed. As a result of studying the surface morphology (SEM images), element composition (EDS spectra), structure (XRD) and optical properties (optical emission, Raman displacement and photoluminescence spectra) of these layers, the crystalline structure of hexagonal modification and their optical and electrical properties have been found to be suitable for use in solar cells.

- The design of a new device with a glass/In_2O_3:Sn/CdS/CdTe structure, a hybrid of a solar cell and an electric battery, and its detailed preparation methodology have been developed.

The scientific novelty of the research:

- Methods for obtaining nano-porous Al_2O_3 (AOA) layers were developed, their formation mechanisms were determined and surface morphology, optical properties, element composition were characterized by various methods.
- A method for obtaining glass/In_2O_3:Sn/Al structures by a multi-stage process using radio-frequency magnetron sputtering in a vacuum spttering device of Leybold Hereaus Z550 brand has been developed.
- For the first time, the dependence of the optical and electrical properties of In_2O_3:Sn sheets precipitated by magnetron spttering in different ratios (0, 5 and 10%) of oxygen/argon gas mixture and annealed in air and argon gas media in the temperature range 200-500^{o}C was studied.
- For the first time, methods for obtaining CdTe and CdS thin films and nanostructured structures in various electrolytes by electrochemical deposition on nickel plate electrodes and glass/In_2O_3:Sn substrates were developed and their electrophysical, structural and optical properties were studied.
- Construction of a new device with a Glass/In_2O_3:Sn/CdS/CdTe structure, a hybrid of a solar cell and an electric battery, and a detailed methodology for its development.

The theoretical and practical significance of the research:

The obtained scientific results allow predicting the basic parameters and photoelectric properties of CdS/CdTe hetero systems composed of electrochemically grown CdS nanosomes within the Al_2O_3 array. The knowledge gained from InSnO/AAO/CdS/CdTe nanostructures on the diffusion of additives, charge mechanisms, and the properties of photoelectric processes provides the basis for optimizing device structures based on these materials.

Approbation and implementation:

Dissertation materials were discussed at the following international and national conferences: The V International Conference Perspectives of Peaceful Use of Nuclear Energy, November 21-23 (Baku, Azerbaijan 2012); Euro Intelligent Materials, 26-27 september (Kiel, Germany 2013); "International Baku Forum of Young Scientists Dedicated to the 90-th Anniversary of National Leader Heydar Aliyev", 20-25 may (Baku, Azerbaijan 2013); 1st International Scientific Conference of Young Scientists and Specialists "The Role of Multidisciplinary Approach in Solution of Actual Problems of Fundamental and Applied Sciences (Earth, Technical and Chemical)", 15-16 October (Baku, Azerbaijan 2014); 31st European Photovoltaic Solar Energy Conference And Exhibition "The Innovation Platform For The Global PV Solar Sector", 14-18 September (Hamburg, Germany 2015); International Conference on Chemical Science and Applications (ICCSA-2016), 6-9 August (*Alexandria, Egypt 2016*); Modern Researches And Prospects of Their Use in Chemistry, Chemical Engineering and Related Fields "The Conference is Dedicated to the 60-th Anniversary of R.Agladze Institute of Inorganic Chemistry And Electrochemistry", September 21-23 (Ureki, Georgia 2016); Qafqaz University, IV International Scientific Conference of Young Researchers "Dedicated to the 93-th Anniversary of the National Leader of Azerbaijan, Heydar Aliyev", 29-30 April (Baku, Azerbaijan 2016); VI Международная Научно-Техническая конференция "Альтернативные Источники Сырья и Топлива АИСТ – 2017", 30 мая-1июня (Минск, Беларусь 2017);

“Metallurgiya və Materialşünaslığın Problemləri” Mövzusunda 2-ci Beynəlxalq Elmi-Texniki Konfrans, 28-30 Noyabr (Bakı, Azərbaycan 2017); Magistrantların və Gənc Tədqiqatçıların “Fizika və Astronomiya Problemləri” Beynəlxalq Elmi Konfransı, 24-25 May (Bakı, Azərbaycan 2018); Academician G.B. Abdullayev Centenary International Conference and School “Modern Trends in Condensed Matter Physics (MTCMP-2018)”, September 24-26 (Baku, Azerbaijan 2018); XXV Международная Научно-Техническая Конференция по Фотоэлектронике и Приборам Ночного Видения, 23-26 мая (Москва, Россия 2018):

Publications: The whole contents of the dissertation are published in 26 scientific works of the author, the list of works is published at the end of the abstract.

Volume, structure and the main content of the dissertation:

The dissertation consist of the introduction, four chapters, results and the list of 162 used references. The scope of the work consists of 241860 characters, excluding 59 figures, 9 tables, graphs, appendices and references.

CONTENT OF WORK

In the introduction has been justified the relevance of the topic, the purpose of the work, scientific novelty, the main provisions for the defence are presented as well as the information about the international and national conferences are shown where the results of the work were discussed. Scientific and practical significance of dissertation and the short description of the chapters also presented in this section.

Chapter One Aluminum, In_2O_3:Sn, CdS and CdTe obtaining methods are reported, their advantages and disadvantages are highlighted. Devices of made on the basis of the materials and devices are described. The anodization process of metals has been used by industry to protect metal components from corrosion for approximately 90 years. During this electro-chemical process the surface chemistry of the metal is changed, via oxidation, to produce an anodic oxide layer that is thick enough to stifle further oxidation.

Aluminum metal (Al), because of its high strength to weight ratio, has found numerous engineering applications and as early as the mid 1920s components on seaplanes used in aviation transportation were being anodized in chromic acid. Two types of anodic Al oxide exist; the first is a non-porous barrier layer that is thin, hard, wear resistant and behaves as an electrical insulator. The second, a thicker porous oxide structure, is called the anodic aluminum oxide (AAO) layer. This layer structure has a high aspect ratio and consists of a porous structure. In engineering applications, this pore structure must be sealed to prevent corrosion. Oxide layers generated during anodization can also be produced on materials such as: magnesium (Mg), niobium (Nb), silicon (Si), tantalum (Ta), tin (Sn), titanium (Ti), tungsten (W), zinc (Zn) and zirconium (Zr).

In recent years, there has been a renewed interest in AAO layers for use as templates in a variety of nanotechnology applications. This is due to the highly controllable pore diameter and cylindrical shape, their periodicity and their density distribution. Using the conventional anodization process the arrangement of the pores is quite disordered, however Masuda *et al*. in 1998, using a two-step anodization process was able to produce a highly ordered hexagonal pore structure from a set of pre-arranged macroscopic parameters. These controllable macroscopic parameters dictated the resulting nano scaled structure that is formed in the AAO layer, thus producing a nano array that can be used in a variety of nanotechnology applications. In the last decade, there has been a veritable explosion of ideas for the potential applications of nano-structured materials. To date, almost all traditional methods of producing synthetic materials have been revisited and investigated for possible use in the manufacture of nanomaterials. Nanomaterials are materials with basic structural units, grains, particles, tubes, spheres, fibers or other constituent components in the range of 0.1 nm to 100 nm. They are increasingly becoming the subject of many investigations in several fields such as materials science, biotechnology and biomedicine. Nanomaterials can be made from a wide range of solid materials such as metals, ceramics, polymers, organic materials and composites. They can come in a wide range of morphologies namely spheres, rods, tubes and plates. In addition, these materials can be grown or self-assembled to replicate the dimensions of natural entities such as collagen fibers. The use of aluminum template for the processing of nanostructures is economically suitable. This technique is highly reproducible and can be achieved in a clean laboratory in a general laboratory.

The term “transparent conducting oxide (TCO)” refers to heavily doped oxide semiconductors that have a band gap sufficiently large (≥3 eV) to make them transparent over the visible spectral range and a conductivity high enough such that they exhibit metal like behavior. Due to their high conductivities, the films also show high reflectivity in the near infrared.

During the last thirty to forty years, the dominant TCOs have been tin oxide (SnO_2), indium oxide (In_2O_3), indium tin oxide (In_2O_3:Sn or ITO), and zinc oxide (ZnO), which have found applications in wide areas of electronic and optoelectronic fields.

Stoichiometric In_2O_3 is a transparent intrinsic semiconductor that can be doped by substituting Sn for In to yield *n*-type indium tin oxide (ITO), a well-known transparent semiconductor. ITO films are particularly attractive in applications such as liquid crystal displays, transparent electrodes of solar cells, and photodetectors.

Some A^2B^6 semiconductors are widely used as buffer sheets on photovoltaic devices. Since the A^2B^6 semiconductor has a n-type conductivity with the band gap of the cadmium sulfide at room temperature, $E_g = 2.42$eV is more important than others as the buffer sheet. Therefore, CdS thin layers can be a "window" for solar cells. From this point of view, CdS is economically cheaper and easier to obtain as a thin layer with high efficiency. Cadmium sulfide has two modifications: sphalerite type cubic structure (α-modification) and hexagonal structure of vursit type (β -modification). The cubic structure of the sphalerite can be considered as a structure consisting of cubic structure that pass into one of two tightly packed with a parameter of a = 6.820 Å. In this structure, each atom of a given species (Cd or S) is associated with atoms of another type (S or Cd) with four atoms in the right tetrahedron hills at a distance of ¾ a. The specificity of this structure is that there is no center of inversion, which results in the fact that (111) surfaces are composed entirely of cadmium atoms and surfaces of ($\bar{1}\ \bar{1}\ \bar{1}$), that is, the crystallographic polarity of the languages.

In this section, CdTe thin film obtaining technologies - Physical vapour deposition, Close space sublimation, Vapour transportation depositions, Magnetron sputtering, Electrochemical depositions, Metal organic chemical vapour deposition, Deposition of spraying methode and Printing methode were discussed. CdTe is a semiconductor compound belonging to the A^2B^6 group, its optical zone is almost optimal for the solar spectrum. The CdTe band gap zone of E_g = 1.5 eV and a high absorption coefficient of $5 \cdot 10^5$/cm indicate that its high quantum output is observed at wide wavelengths from the ultraviolet area to the barrier zone (λ = 825 nm) of CdTe.

At the end of the chapter, the existing literature examining the issues to be solved in the dissertation is determined.

The **second chapter** deals with the methodology of the experiment. Here are described obtaining of Indium Stanum Oxide (In_2O_3:Sn) and Aluminum by the device of Leibold Herause Z550 with magnetron sputtering method, research of their optical properties, aluminum oxidation methods, obtaining technology of electrochemical and close space sublimation methods in accordance of CdS and CdTe, study their optical, structural and photoelectric properties.

The radio freguency (RF) power using of magnetron sputtered ITO films have been deposited by In and Sn content of 9:1 ratio, which is equipped with a standard target with the addition argon-oxygen (Ar-O_2) mixture in vacuum chamber of Leybold Herause Z550. DC method cannot be used to sputter nonconducting targets because of charge accumulation on the target surface. This difficult can be overcome by using RF sputtering. A single rf sputtering apparatus can be used to deposit conducting, semiconducting, and insulating coatings. RF reactive sputtering offers a number of advantages compared with other techniques such as CVD and PVD: it is possible to predict the layer structure and thickness; compound materials may be sputtered roughly without losing the target stoichiometry; good adherence and high film density can be achieved because of the high kinetic energy of the incident target atoms; and uniform layer thickness are obtained.

Prior to conducting the magnetron vacuum deposition process, ion purification was carried out in a vacuum chamber with a pressure of $8 = 10^{-1}$Pa at power of 200-500 W and t=2min to clean the surface of the sample and target. Subsequently, Al deposition process was carried out under the power of 100-150 W gas discharge conditions depending on the thickness of the aluminum layer, which was not broken down without vacuuming. The aluminum wire was used as a working material, as a heating element is heated tungsten spiral at power of 160W and current of 40A used for to get thin layers of aluminum by thermal evaporation method. The evaporation process consists of several stages. First, aluminum wire is placed in the center of the tungsten spiral. Then the aluminum wire begins to melt as the spiral current flow increases slowly. Melting wire is attached to the center of the spiral. In further growth of the flow current, the molten aluminum spiral is fully covered and evaporation starts at a very low speed.

The mechanism of electrochemical oxidation of aluminum foil and aluminium thin layers which deposited on various substrates by magnetron sputtering method has been shown in different solutions and in different modes. A 2-electrode chemical bath was developed and prepared for obtaining nanoporouse Al_2O_3 (AAO) layers. In this device uses a Pt wire as an auxiliary electrode - cathode, and an anode, directly using Al plate. Thermoelectric refrigerator or ice are used to cool the insulation solution to temperatures of 3-5ºC. During the anodization process, a high-speed electric micro-engine was used to mix the solution.

Cadmium sulphide semiconductor thin films are made of aqueous electrolyte with 0.125M $CdSO_4$, 0.25M Na_2SO_3, 0.35M H_2SO_4, 0.007M Trilon-B ($C_{10}H_{14}O_8N_2{:}H_2O$), and ethylene-glycol at temperature $T = 130^0C$, 0 C , and anhydrous solution of 0.1MNH_4Cl was used. In the first solution electrochemical deposition process was carried out on Ni, glass/In_2O_3:Sn and glass/In_2O_3:Sn/AAO electrodes with a visible surface of 2 cm^2. The joint deposition process was performed in a three-electrode electrolysis bath at different potentials under potentiostatic conditions. In the second solution, the electrochemical deposition at T = 90-100^0 C is carried out in a potentiostatic mode in a two-electrode electrolysis bath.

CdTe thin layers were obtained by two methods: 1) Close space sublimation and 2) Electrochemical deposition. Deposition of CdTe thin layers using close space sublimation method by the Two-Zone Furnace for PVD (CSS) Processing - Middle-range Sublimation Unit OTF-1200X-RTP-II, MTI, USA. For close space sublimation (CSS) of CdTe was used as a source of pure ceramic powder with a thickness of 100–200 μm, which was placed in a ceramic volume up to the base of the bottom. Electrochemical deposition was performed on the submerged layers of CdTe with a two-electrode spraying system consisting of a cathode-like glass/In_2O_3:Sn working electrode and a high-purity carbon electrode inserted into the electrode. The electrochemical method was prepared using 1.5m $CdSO_4$ solution of 1000mg/L $CdCl_2$ and 1mM TeO_2 with low concentration for dissolution of CdTe. The deposition process was carried out using the IVIUMSTAT electrochemical analyzer potentiostat, cathode polarization curves were plotted, and the deposition potentials of CdTe to different substrates (ITO and CdS) were determined.

X-ray analysis of the layers using CuKα (λ = 1.54060 Ǻ) diffractometers of Rigaku Miniflex-500 and X-Ray diffractometer D2 Phaser (Bruker, Germany), The morphological analysis of the surface was characterized by Smart SPM 1000 AIST NT atomic force microscope, Carl Zeiss Sigma scanning electron microscope (SEM), and energy dispersion spectra (X-ray EDS) by Oxford Instruments SEM. In_2O_3:Sn (İTO) deposited by magnetron physical sputtering on a glass substrate and optical transmission and absorption spectra of electrochemically deposited samples measured on a Specord 250+ UV / VIS Spectrophotometer, Raman and photolumensis spectra measured using a spectroscope of Nd: YAG (λ = 532nm) Tokyo instruments Nanofinder 30-NM01 (Tokyo Instruments, Inc.) device. The characteristics of the solar cells were measured using the Solar cell I-V Tester Model IV16K (PV Mesurements Inc, USA) solar simulator. The thickness of the layers was measured on an MII-4 interference microscope and on a Rotating Compensatory Ellipsometer M2000-DI (J.A. Woollam Co.Inc. USA) ellipsometry device. The resistivity of the samples, mobility and the conductivity type were measured by the Van-Der-Pau method using a standard 4-probe device and a thermal probe.

In **chapter three** dedicated to X-ray structure, electrophysical, optical, photoelectric and photoluminescence properties of nanostructured glass/In_2O_3:Sn/AAO/CdS/CdTe whole and separately structures from the layers that make it up.

First, the results of the study of the dependence of the structural, optical and electrical properties of In_2O_3:Sn, the primary layer of this structure, on the composition of the oxygen/Ar mixture in the magnetron chamber are presented. In the absence of oxygen in the magnetron chamber (O2 = 0%) in the X-ray diffraction pattern (Figure 1) of the layers obtained by magnetron sputtering in 0% and 5% oxygen/argon gas mixture and then annealed in air at 200, 400 and 500°C and then in the diffractogram of the layers annealed at T=200°C in an Ar gas environment in a muffle furnace, diffusion "cohesiveness" characteristic of amorphous materials in the range of angles $2\theta=18\div38°$ is observed. Its presence in this structure indicates the presence of amorphous phase materials (including amorphous glass substrates). Increasing this temperature as a result of annealing of the structure at gradually increasing temperatures (200-500°C) leads to both narrowing of the diffraction peaks and an increase in intensity. The ratios of the peaks of the In_2O_3:Sn diffraction spectra characteristic of surfaces (222) and (211) in the annealed layers at T=500°C give the values of 4.8 (J222 / J400) and 3.7 (J211 / J400) of the intensities of the weakest (400) peaks. Estimation of the size of crystallite particles in the layer by the Debay-Scherrer formula showed that they are ≈13nm.

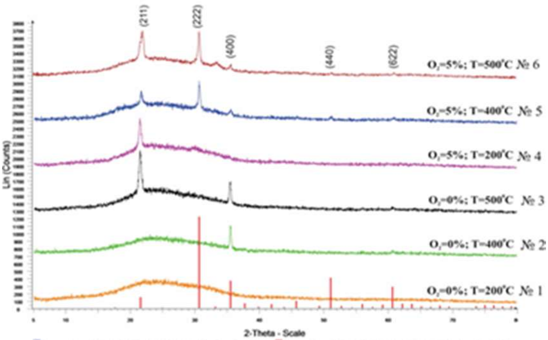

Figure 1. Diffractogram of In_2O_3:Sn layers annealed at 0, 5% oxygen at 200, 400 and 500°C.

As can be seen from the images of the In_2O_3:Sn layer obtained by atomic force microscopy and the histogram of the geometric distribution of these particles (Figure 2), their size varies between 5 nm and 20 nm, and the maximum histogram is 11.9 nm. This confirms the figure obtained according to the diffractogram and the Debay-Scherrer formula.

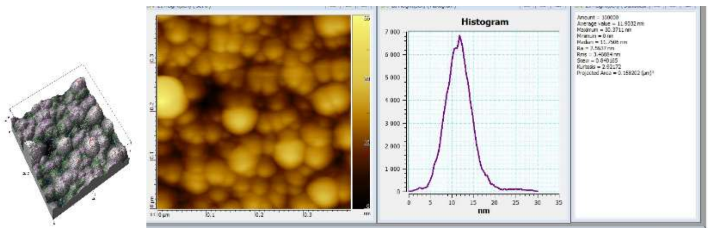

Figure 2. Imaging of In_2O_3:Sn layers by atomic force microscope and histogram of dimensional distribution of crystallites.

Then the analysis of optical properties of these layers is given. It is shown that, the transparency of the In_2O_3:Sn layers does not change significantly with the addition of q_{O_2} = 5% oxygen in the deposition chamber q_{O_2}= 0% (T = 60%), but the amount of oxygen q_{O_2}= 10% its transparency increases dramatically (T = 90%). But, after the annealing of the samples at 500ºC, obtained under the condition of q_{O_2} = 0% the transparency of the layers increases compared to the before annealing (T = 80%). On the other hand, the transparency of In_2O_3:Sn is reduced relative to that by adding q_{O_2}= 5% oxygen (T = 75%), and the absorption edge of the spectrum is shifted to a short wavelength of 300-450 nm. At the same time, the optical emission rate of argon-treated samples after 10 minutes of annealed at 400ºC in argon gas and air environments of these layers is higher than in air-treated samples. The decrease in the transparency of the layer can be explained by the fact that during the annealed in the air, the oxygen in the air reacts with In2O3: Sn and enters its lattice.

The role of partial pressure of oxygen in a vacuum magnetron chamber in the concentration, mobility and electrical conductivity of carriers is then determined by analyzing the electrophysical properties of the In_2O_3:Sn layers. It is shown that when the partial pressure of oxygen varies between (10^{-4}-10^{-5}) torres, the electron mobility increases, while the concentration and conductivity of the charge carriers decrease. Each vacancy of oxygen can contribute to the conduction of two free electrons. As the partial pressure of oxygen increases, the number of oxygen vacancies increases and the concentration of carriers decreases. On the other hand, the lack of oxygen in the layers increases the concentration of electrons, which in turn leads to a decrease in their absorption and transmission, narrowing of the band gap, weakening the effectiveness of the Sn addition and a decrease in the charge of the carriers. The decrease in the speed of the carriers is explained by the increase in their more effective dispersion on ionized additives.

The next section analyzes the mechanism of formation of the AOA nanoporous structure synthesized by oxidation at the anode on the basis of aluminum deposited by magnetron sputtering on the second layer of this structure, glass/In_2O_3:Sn. It also presents SEM images of AOA nanopores, element composition corresponding to stoichiometry determined on the basis of energy-dispersive analysis (EDS), and optical transmission spectra measured in the visible light range. Figure 3 shows the current-time dependence observed during the formation of porous Al_2O_3 templates (molds) during the oxidation process at the anode. As can be seen from the graph, this process consists of four different stages, as shown below. In the initial (1) stage, the current strength is high at first due to the high conductivity of the aluminum surface. The O_2 and OH ions then diffuse to the Al surface to form the Al_2O_3 oxide layer (AOA) on the Al surface, which is accompanied by an increase in resistance and a sharp decrease in current. In the second (2) stage, the newly formed oxide layer gradually dissolves in the electrolyte and nanopores begin to form on its surface. As a result, the oxide layer becomes thinner, its resistance decreases, and the current begins to increase. In the third stage (3), the processes of oxide formation and dissolution are balanced, and at the same time, self-regulating pores are formed in the layer. During this phase, the anode current remains relatively constant and can therefore be called the stabilization phase. This stage can take several seconds or minutes, depending on the thickness of the Al layer. In the fourth (4) stage, the whole layer of Al gradually oxidizes, the resistance of the layer increases, and the anodization current decreases to zero. It has been found that the applied electrical voltage, electrolyte temperature and oxidation time, which are the oxidation parameters at the anode, have a definite effect on the diameter, thickness and regularity of the pores in the AOA.

Figure 4 shows the SEM description and photographs of the AOA surface we obtained. It can be seen from the SEM description that the number of adjacent pores in the immediate vicinity of each pore is 6, and when combined with imaginary lines, a regular hexagon with internal angles $\approx$ 125-127º is obtained. In the photo, the AAO layer, which is actually optically transparent, appears purple as a result of interference. Interference confirms that it is highly regulated. The highly self-aligning arrangement of the pores can also be seen in the AFM images.

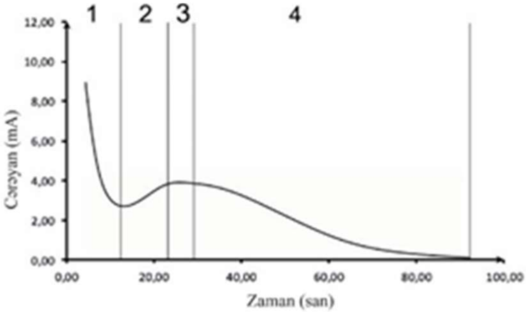

Figure 3. Time dependence of current in the oxidation process.

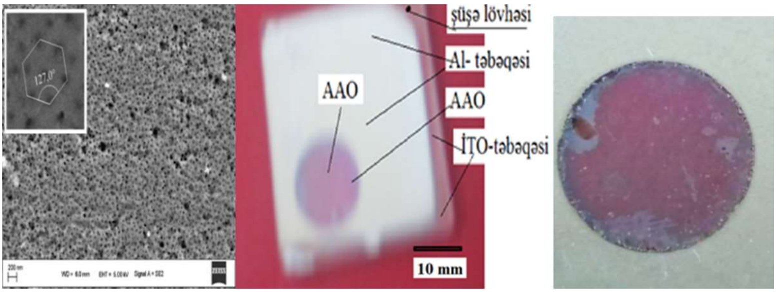

Figure 4. SEM image of AAO layer (X50,000) (left) and photograph of In2O3: Sn / AOA structure synthesized on glass (center and right)

Then the optical transmission spectrum of nano-porous AOA is presented. It is shown that the AOA layer is sufficiently transparent to sunlight (T=60-70%). He also presented the EDS spectrum and element composition of the oxidized AOA layer obtained by SEM at the anode and showed that the chemical element composition of the layer is stoichiometric.

The next section presents the results of the study of the method of obtaining nanostructured CdS, the crystalline structure, element composition and optical properties of the planar thin layer, which is the 3rd layer of the structure, and grown in the pores of the AOA. In order to determine the mechanisms of the process of electrochemical deposition of CdS layers on various materials, the initial deposition was carried out on Ni electrodes using the electrochemical analyzer potentiostat brand IVIUMSTAT. The results of the study of this relatively inexpensive process have been used as a model for determining the mechanisms of deposition of CdS nanotubes into AOA pores in the glass/In_2O_3:Sn/AAO structure. Ethylene glycol electrolyte containing Cd ions and S molecules dissolved in the form of colloidal particles was taken as the polar electrolyte for the precipitation of CdS. Sulfite electrolytes containing Cd ions were used as inorganic electrolytes. The electrolytic precipitation potential area of Cd and S, the main components of the selected electrolyte, was determined separately, and the kinetics and mechanism of the process were clarified.

The X-ray diffraction pattern of the Glass/In_2O_3:Sn/CdS structure is then analyzed (Figure 5). It was determined that 2 of the 16 peaks of different intensities present in this diffractogram belong to In_2O_3:Sn (the graph below shows the In_2O_3:Sn diffractogram). The remaining 14 peaks consist mainly of CdS nanocrystals with a hexagonal modified crystalline structure with a stoichiometric composition and a small amount of CdO and cubic modified CdS additives. Analysis of the most intensive (No. 3) peak based on the Debay-Sherer formula found that the average size of CdS particles was ~ 23 nm.

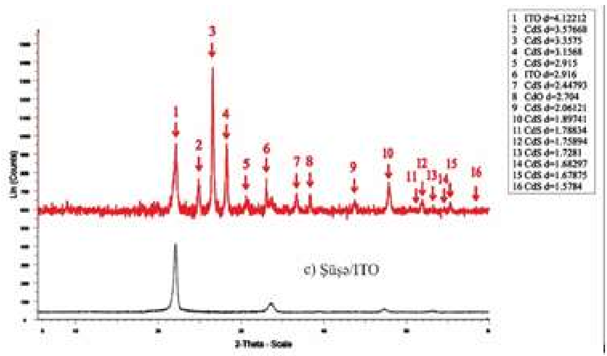

Figure 5. Diffractogram of glass/In_2O_3:Sn/CdS layers.

The layers have n-type conductivity and a specific conductivity of 16–20 Ohm•cm. The EDS spectrum and chemical element composition of the samples, as well as SEM micro-images and photographs (Figure 6) show that these layers are composed of densely packed large particles with a stoichiometric composition, deposited along the substrate at the same thickness (200–500 nm, depending on sedimentation time). . The layers have a high optical emission (T ~ 70%) of light in the wavelength range of 400-800 nm.

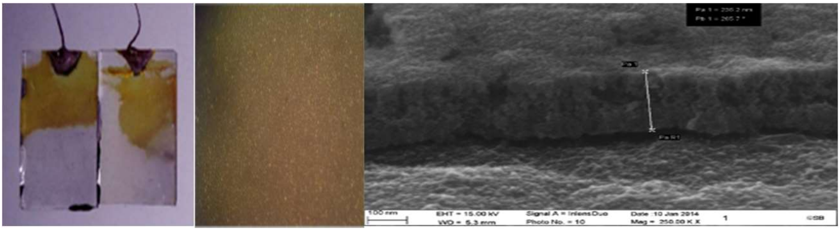

Figure 6. Photograph of CdS deposited in glass/In_2O_3:Sn/Al_2O_3 templates.

The Raman shift spectra of the thin layer of CdS annealed at 500°C in the air and of the Al_2O_3/CdS structures annealed at 100-300ºC are then analyzed (Figure 7). In the spectra, the first order of CdS with a hexagonal modification of the wave number at ~ 300cm^{-1} corresponds to the longitudinal optical phonon (1LO) mode, and the second order of ~ 605cm^{-1} corresponds to the cubic (sphalerite) modification of the second order length (2LO) peaks corresponding to the optical phonon mode are observed.

This spectrum, on the one hand, confirms the results obtained on the analysis of X-ray diffractograms on the crystal structure of CdS, and on the other hand, shows that the relative magnitude of the hexagonal phase is many times greater than that of the cubic phase. In addition to the 299 cm^{-1} peak in the Al_2O_3/CdS spectra, there is also a peak related to Al_2O_3 at 476.8 cm^{-1}. As can be seen from the spectra, the heat treatment temperature has a strong effect on the crystalline perfection of CdS.

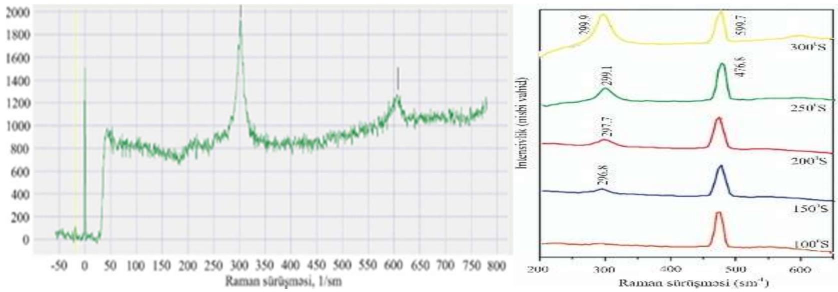

Figure 7. Raman spectra of annealed at 500°C (left) and at 100, 200, and 300ºC (right).

At a temperature of 100ºC, there is a peak of 476.8 cm^{-1} specific to Al_2O_3 in the spectrum of the annealed structure, but no peak related to CdS. CdS-specific 1LO peaks are only visible in the spectra for temperatures above 150ºC. The absence or weak intensity of the peak in the untreated CdS is due to its amorphous or imperfect crystallinity. As the processing temperature increases, the intensity of the 1LO peak increases and slightly shifts towards larger wave numbers (296.8 cm^{-1} at 150°C and 299.9 cm^{-1} at 300°C). These are the result of the combined effect of the effect of temperature on the growth of CdS-nanoparticles in the Al_2O_3 pores and the increase in crystal perfection, as well as the pressure of the Al_2O_3 matrix on the crystal lattice of CdS and the measurement effect.

The photolumenic spectrum of the laser-excited nanostructured CdS layers with a wavelength of 532 nm is then analyzed (Figure 8). An emission band covering the range of 500-1000 nm and a maximum of about 760 nm is observed in the spectrum. Diameter of CdS nanotubes synthesized by us (40-60 nm).

It has been shown that in synthesized CdS nanotels, large length / diameter ratios are large and they have a high number of surface and subsurface defects. According to the results of other researchers, the peaks in our results are also related to the emission of traps caused by these defects.

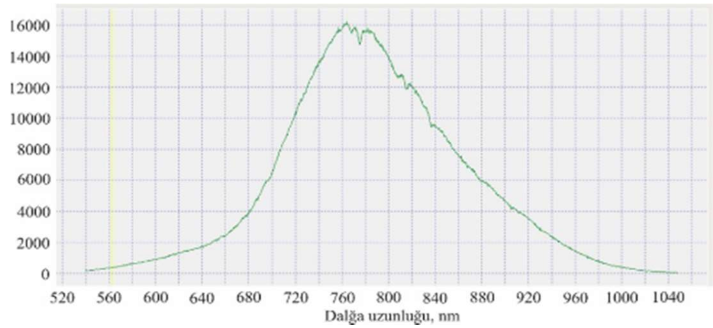

Figure 8. Photolumensis spectrum of CdS layer.

The next section presents X-rays, AQM, and SEM images of CdTe obtained by electrochemical precipitation and close-range sublimation, the last layer of this structure. Sulfate-tartrate electrolyte was selected for electrochemical precipitation of CdTe nanostructures. During the electrochemical deposition, cathode polarization curves were plotted and the deposition potentials of CdTe to different substrates (InSn:O and CdS) were determined. Based on the radiograph, it was shown that the thin layers of CdTe crystallize with a sphalerite-type cubic structure (space group F43m) with a lattice parameter a = 6485 Å. The CdTe layers have a superior orientation along the direction (111). Its grains are packed in six packages and have an average size of 300 nm.

Chapter Four discusses based on the nanocell CdS grown in the pores of AAO, the design of a new device, which is a hybrid of Glass/In_2O_3:Sn/CdS/CdTe nano-structured solar cell and an electric battery, and its detailed preparation methodology were presented. It also discusses the electrophysical and photoelectric properties of the solar cell based on heteroconducting nano-CdS/CdTe layers.

The new hybrid device consists of a nanostructured PV solar converter and a nanocapacitor mounted on the front and back surfaces of a single transparent glass plate coated with an In2O3: Sn layer on both sides.

Based on the theoretical model of CdS/CdTe heteroconducting solar cells, the window layer was evaluated for the efficiency of CdS

/ CdTe heteroconductive solar cells based on the traditional CdS thin layer and nanocells grown in the AAO matrix. It has been shown that the optical absorption edge in conventional thin layers of CdS corresponds to a wavelength of 512 nm, and the absorption edge from CdS nanotels grown in AAO pores corresponds to 480 nm. Therefore, the relative increase in photocurrent (from 22.4 mA / cm2) is due to the fact that the energy of the photons used in the depleted region of the CdS / CdTe heteroconductor, which is free of CdS-wires of the AAO matrix with a porosity of more than 50% and penetrates through the transparent field, is higher than the traditional CdS window layer. 26.1 mA / cm2) is 17% higher.

Volt-ampere characteristics of the glass/In_2O_3:Sn/Al_2O_3/CdS/CdTe structure are then analyzed in the dark and at AM1.5 (air mass 1.5) (~150 mV / sm^2) lighting conditions. The open circuit voltage, short-circuit current density and charge factor, which are the parameters of the solar cell, reached 705mV, 25.3mA/sm^2 and 36.4%, respectively. These elements were also compared with traditional thin-layer CdS/CdTe solar elements under the same conditions.

MAIN RESULTS

1. The reason for the decrease in conductivity with increasing oxygen fraction, observed in thin layers of In_2O_3:Sn obtained by oxygen / argon gas mixture (0, 5 and 10%) in a medium of magnetron dusting and thermally treated in the temperature range of 200–500°C, is that in In_2O_3:Sn is associated with a decrease in the concentration and mobility of carriers as a result of the formation of acceptor-type Sn vacancies.
2. A thin layer of aluminum deposited on glass substrates coated with a thin layer of In_2O_3:Sn has optically transparent and dielectric properties by self-oxidation at the anode, has a self-regulating structure, pores with a diameter (5–100) nm depending on the conditions of production, and a thickness of 300 nm ÷ Interchangeable at 1mkm intervals, the technology of cultivation

of Al_2O_3 (AOA) layers has been developed, the mechanism of oxidation process has been determined, their surface morphology, structure, optical properties (transmission and raman shift spectrum) and element compositions have been characterized by different methods.

3. The technology of electrochemical precipitation of CdS layers obtained on the Glass/In_2O_3:Sn/AAO structure has been developed. As a result of studying the surface morphology (SEM images), element composition (EDS spectra), structure (XRD) and optical properties (optical emission, Raman displacement and photoluminescence spectra) of these layers, the crystalline structure of hexagonal modification and their optical and electrical properties have been found to be suitable for use in solar cells.
4. The electrolyte composition and electrolysis conditions required for the electrochemical extraction of CdS layers were determined, as well as the potential area for joint deposition. The precipitation potential area of cadmium ions in the selected electrolyte solutions was determined, along with the precipitation potential area of sulfur ions, their deep reduction potential area up to sulfide ions was determined.
5. Methods for obtaining nano-porous Al_2O_3 (AOA) sheets have been developed, their surface has been characterized by SEM, various methods.
6. A method for obtaining glass/In_2O_3:Sn/Al structures by a multi-stage process using radio-frequency magnetron dusting in a vacuum dusting device of Leybold Hereaus Z550 brand has been developed.
7. For the first time, methods for obtaining CdTe and CdS thin films and nanostructured structures in various electrolytes by electrochemical deposition on nickel plate electrodes and glass/In_2O_3:Sn substrates were developed and their electrophysical, structural and optical properties were studied.

8. The design of a new device, a hybrid of a solar cell with Glass/In_2O_3:Sn/CdS/CdTe structure and an electric battery, and its detailed preparation methodology have been developed.
9. Based on the VA characteristics of the CdS/CdTe nanostructure measured under AM-1.5 (~ 150 mV/sm^2) lighting conditions, it was determined that the energy conversion efficiency in solar cells is 6.5%, open circuit voltage 705mV short-circuit current density 25.3mA / cm2 and charge factor It is at the level of 36.4%

The main results of the dissertation were published in the following works.

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