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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

ELECTRONIC PROPERTIES OF ZnS(Se)-ZnTe SYSTEM THIN FILMS AND THEIR BASED STRUCTURES

Specialization: 2211.01 - Solid state physics

Field of science: Physics

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The dissertation work was carried out at the Institute of Physics of the Ministry of Science and Education of the Republic of Azerbaijan, at the Department of Semiconductor Physics of the Faculty of Physics of Baku State University and at the center "DAYTAM" (East Anadolu Higher Technology Application and Research Center) of Ataturk University of the Republic of Turkey.

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GENERAL CHARACTERISTICS OF WORK

Relevance of the topic and degree of development. The fulfillment of the increasing demand in electronic technology relies on the complex approach that combines the partially disordered structures of chalcogenide-based compound semiconductor heterojunctions and their delicate layers' electron properties complex research. In the field of electronics, the possibilities of preparing delicate layers in a simple and cost-effective manner are determined by a complex approach that combines their high efficiency. On the one hand, it involves the exploration of new materials and their delicate layers' utilization, and on the other hand, the improvement of the technology for obtaining delicate layers of existing complex-structured semiconductors, as well as their parameters' preservation at a high level through a simpler technology, demands expansion of research in this area.

In this regard, the technology of chemical obtaining of delicate layers from aqueous solutions attracts special attention. There are several variations of this method: direct formation of layers in aqueous solution, immersion of the substrate in the solution with a high electric field or by pulverization, electrochemical deposition, etc. The prospects of the chemical obtaining method depend on several factors: obtaining layers of complex-structured semiconducting materials, obtaining various semiconducting thin films and delicate layer composites, introduction of active impurities, preparation of multilayer structures, formation of electrical contacts, realization of metal-semiconductor contacts and heterojunctions using a unified technology, epitaxy of nano-sized layers of the same material on a massive substrate, application of micro- and nanomaterials, etc. This method allows for the efficient realization of the serial production of various metals' chalcogenide compounds with unique properties in the form of delicate layers and large-scale surfaces and expands the application areas of these materials.

Research in this direction shows that the efficiency of such structures is determined not only by the generation-recombination processes but also by the technological and design features of the

contact materials' selection and obtaining.

Therefore, the determination of technological regimes that allow for the production of delicate layers with high sensitivity based on ZnS and ZnSe, the investigation of phenomena combined with significant scientific-theoretical and practical-technological effects such as optical absorption and photoconductivity in the obtained layers and structures, and the creation of metal-semiconductor and semiconductor-semiconductor structures based on these materials are currently relevant.

Research goals and objectives.

The purpose of the dissertation work is to investigate the fundamental characteristics of electron processes and current transport mechanisms in nanostructured layers based on ZnS(Se)S(Te) obtained by chemical and electrochemical deposition methods, as well as to determine their practical application possibilities.

To achieve this goal, the following tasks have been set and solved:

1. Determine the dependence of the physical properties of delicate $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ layers on the deposition and thermal annealing regimes to identify the optimal conditions for obtaining layers with the necessary parameters.

2. Comparative investigation of the properties of nano-sized $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ layers and nanoparticles obtained by chemical and electrochemical deposition methods, depending on the composition and deposition regimes.

3. Clarify the mechanisms of relaxation and recombination processes in $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ nanostructured layers depending on the dimensions of nanoparticles.

4. Determine the optimal composition and thermal treatment conditions of Si-mes.Si/CdS structures obtained on silicon substrates to enhance the photo and gas sensitivity efficiency.

5. Investigate the possibilities of preparing photodetectors with high sensitivity based on p-Si/$ZnS_{1-x}Se_x$ and p-Si/$ZnSe_{1-x}Te_x$ heterojunctions by controlling the electrochemical deposition and thermal annealing regimes.

6. Study the effect of doping on the electrical properties of p-Si/$ZnS_{1-x}Se_x$ and p-Si/$ZnSe_{1-x}Te_x$ heterojunctions in KOH + C_3H_8O and HF+HNO_3 solutions.

7. Investigate the effect of thermal treatment on the photoelectric properties of p-Si/$ZnS_{1-x}Se_x$ and p-Si/$ZnSe_{1-x}Te_x$ heterojunctions under various environments and conditions.

8. Explore the possibilities of preparing photodetectors with high sensitivity based on ZnS/ZnTe/CdTe/CdS multilayer heterojunctions by controlling the electrochemical deposition and thermal annealing regimes.

Research methods.

Methods of chemical and electrochemical extraction of gentle layers from aqueous solutions, methods of investigating the volt-ampere, volt-farad characteristics of structures based on nanoparticles and nanostructured layers, methods of studying photoconductivity and photoluminescence spectra.

The scientific novelty of the research consists of the following:

1. The optimal composition, deposition, and thermal annealing regime that ensures high sensitivity of $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ nanostructured layers have been determined, demonstrating the superiority of the chemical method over other methods.

2. The mechanism of the observed photochemical reaction in nanostructured $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ layers has been identified.

3. Based on the investigation of the main parameters and characteristics of Si/CdS heterojunctions prepared by electrochemical method, the current transport mechanism has been determined. Changes in the parameters of the heterojunction observed after thermal annealing have been shown to be related to electron-molecular processes occurring in the transition region and at the surface of the layers.

4. It has been determined that the main characteristics of p-Si/$ZnS_{1-x}Se_x$ and p-Si/$ZnSe_{1-x}Te_x$ heterojunctions prepared by electrochemical method are governed by the presence of

generation-recombination processes in the buffer layer, and the volt-farad characteristic indicates the sharp anisotropic heterojunction nature of these structures.

5. The mechanism of the influence of chemical doping on the electrical properties of p-Si/$ZnS_{1-x}Se_x$ and p-Si/$ZnSe_{1-x}Te_x$ heterojunctions has been studied.

6. The mechanism of the influence of S-Se-Te substitution and various thermal treatments in different environments and conditions on the electrical properties of p-Si/$ZnS_{1-x}Se_x$ and p-Si/$ZnSe_{1-x}Te_x$ heterojunctions has been determined.

7. It has been demonstrated that the use of a multi-layered ITO/ZnS/ZnTe/CdTe/CdS structure compared to the bilayer ITO/ZnTe/CdTe heterojunction results in superior efficiency and stability parameters as solar elements.

Practical importance of the work and application of the results:

The theoretical and scientific-practical significance of the dissertation work is determined by the following factors:

The structures prepared based on $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ thin films exhibit economically advantageous and highly efficient photodetectors, solar cells, diodes with high rectification ratios, optoelectronic devices operating in a wide spectral range, and also enable the preparation of micro- and nanoelectronic elements, nanoparticles, and nanomaterials. These capabilities open up possibilities for the development of photo detectors as well as the fabrication of micro- and nanoscale electronic devices.

The main provisions defended:

1. Determination of optimal conditions for obtaining layers with desired parameters based on the investigation of the physical properties of $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ layers, as well as their dependence on the deposition technology and thermal annealing process.

2. Investigation of the size-dependent mechanisms of relaxation and recombination processes in $ZnS_{1-x}Se_x$ and $ZnSe_{1-}$

$_xTe_x$ nanostructured layers.

3. Determination of the optimal composition and thermal annealing regime to enhance the photo and gas sensitivity of Si/CdS structures grown on silicon substrates.

4. Possibilities of preparing high-sensitivity photodetectors based on p-Si/$ZnS_{1-x}Se_x$ and p-Si/$ZnSe_{1-x}Te_x$ heterojunctions by controlling the electrodeposition and thermal annealing regimes.

5. The impact of doping in KOH + C_3H_8O and HF+HNO_3 solutions on the electrical properties of p-Si/$ZnS_{1-x}Se_x$ and p-Si/$ZnSe_{1-x}Te_x$ heterojunctions.

6. The effect of thermal processing in various environments and regimes on the electrical properties of p-Si/$ZnS_{1-x}Se_x$ and p-Si/$ZnSe_{1-x}Te_x$ heterojunctions.

7. Possibilities of preparing high-sensitivity photodetectors based on ZnS/ZnTe/CdTe/CdS multilayer heterojunctions by controlling the electrodeposition and thermal annealing regimes.

The name of the institution where the dissertation work was carried out. The dissertation work was carried out at the Institute of Physics of the Ministry of Science and Education of the Republic of Azerbaijan, at the Department of Semiconductor Physics of the Faculty of Physics of Baku State University and at the center "DAYTAM" (East Anadolu Higher Technology Application and Research Center) of Ataturk University of the Republic of Turkey.

Approval of work: The results of the research included in the dissertation work were discussed and published in the materials of the following Republican and International scientific conferences:

1. Riyaziyyatın tətbiqi məsələləri və Yeni informasiya texnologiyaları, həsr olunmuş "Электронные свойства гетеропереходов p-Si/$ZnSe_{1-x}Te_x$", III Respublika Elmi Konfrans, (Sumqayıt 15-16 dekabr-2016).

2. Turkish Physical Society 30th İnternational Physics Congress-Herodot Cultural Center, "İmprovement of photoelectrical parameters of the Mo-$CuInSe_2$/$Cd_{1-X}Zn_XS_{1-Y}Se_Y$ flexible solar cells", (Bodrum/Turkey September 5-9, 2018).

3. Матеріали конференцій МЦНД, "Determining the effect on heterojunctions by reducing series resistance",

(29.07.2022; Черкаси, Україна).

4. İnternational scientific and practical conference «An ıntegrated approach to scıence modernızatıon: Methods, Models and Multıdıscıplınarıty» 26.08.2022, Vinnytsia, Ukr - Vienna, Aut

Structure and scope of the dissertation. The dissertation is presented on 164 pages of printed text, consisting of an introduction, four chapters, conclusions, practical recommendations, 42 figures and 9 tables, a bibliography of 153 items. In the literature there are 20 works in Russian, 133 works in English.

The volume of chapters of the dissertation consists of 164200 characters, including chapter I 766793, chapter II 2886, chapter III 12204, chapter IV 56317.

Published scientific works. Based on the materials of the dissertation, 14 scientific articles (1 of them were published in Web of Science and 2 in Scopus indexed journals) and 4 theses were published.

MAIN CONTENT OF WORK

In the introduction The relevance of the topic has been justified and the degree of elaboration has been analyzed. The object and subject of the research have been determined, and the goals, objectives, and methods have been specified. The main arguments presented in the defense, the scientific novelty of the research, and the theoretical and practical significance have been explained. The approval and application, as well as the name of the organization where the dissertation work was carried out, have been provided. The structure sections of the dissertation have been indicated separately, with the total volume of the dissertation specified.

In the first chapter This work provides a comparative summary of existing scientific and technical literature on the chemical and electrochemical deposition methods for obtaining thin films of ternary $A^{II}B^{VI}$ semiconductor compounds and their

electrical and photoelectric properties, as well as the preparation of heterostructures based on these thin films using various technological methods. The theory of heterojunctions and their current transport mechanisms is presented.

The analysis conducted has determined that the electrochemical deposition method has been extensively studied only for the fabrication of binary $A^{II}B^{VI}$ semiconductor thin films, while insufficient attention has been given to the technology of obtaining ternary thin films. As a result of the conclusions and analysis performed, the relevance of improving the technological methods for obtaining $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ thin films, as well as conducting in-depth experimental and theoretical studies for structural analysis, has been established. Furthermore, the importance of determining the optical, photoelectric, and luminescent properties of $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$-based thin films has been emphasized.

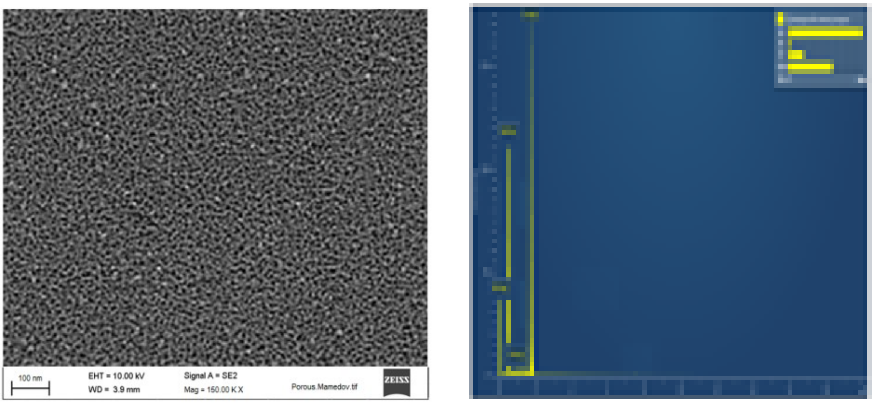
In the second chapter, the doping of Si substrates, surface passivation, and the deposition conditions of $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ thin films were investigated. The cyclic voltammetry characteristics (voltammograms) of the mixture of salts in aqueous solutions were examined, initially separately and then as a mixture with different concentrations and pH values. The cyclic voltammetry measurements were performed in the range of -1.2 to +1.2 V. The characteristics were measured with the application of external voltages, initially negative and then positive, in two different directions.

Monocrystalline p-Si parallel platelets with a thickness of approximately 0.2 to 0.6 mm and a specific resistance of 0.01-0.09 Ω·cm were used as substrates during the electrochemical deposition, with the crystallographic direction being (111). Before being placed in the electrochemical cell, the surface of the p-Si platelets was cleaned from SiO_2 oxide layers and impurities in weak acidic solutions. For this purpose, the p-Si platelets were stored in a $KOH+KNO_3$ (1:4) solution at room temperature for 2 days, followed by sequential treatment in a 10% HCl solution for 3-5 minutes, rinsing in clean ethanol and distilled water. In some cases,

the rinsing of the substrates was carried out in a 300°C or higher temperature HCl solution for a short period of time. Subsequently, the platelets were dried with nitrogen and immersed in an HF:ethyl alcohol (1:1) solution. During the deposition process, a cylindrical Teflon cell with a circular or square-shaped aperture of approximately 1 cm^2 area at the bottom was used. The p-Si substrates were placed on Al foils used as cathodes. To prevent the leakage of the electrolyte from the lower aperture, the Si platelets were tightly attached to the cell using clamps with the help of Teflon washers. Platinum mesh was used as the anode material. To distribute the applied voltage evenly on the surface of the p-Si and in the electrolyte, the platinum electrodes were prepared in a spiral shape. During the deposition process, a $CdCl_2$ aqueous solution was added to the HF+alcohol solution at a ratio of 10:1. The addition of $ZnCl_2$ to the solution increases the possibility of obtaining BS/ZnS structures formed on the Black-Si (BS) basis, along with the stabilizing interaction of Si-Zn complexes, both inside the mesas and on the surface. For comparison purposes, heterojunctions based on BS with and without $ZnCl_2$ addition (BSCd) were investigated in the present dissertation work. For the comparison, the same anode voltage levels of 20, 25, and 30 V were applied to both solutions. The electrodeposition was carried out at a current density of 40-70 mA/cm^2. Depending on the duration of the deposition (30-1800 seconds) and the anode voltage in the solution, BS mesas with dimensions of 7-80 nm were formed on the surface of the monocrystalline p-Si. Increasing the anode voltage allowed for an increase in the mesa size. By keeping the anode current constant (10-40 mA/cm^2) and increasing the anode voltage to 25-30 V, the nature of the deposition process changed significantly. Specifically, under the same conditions and for the same duration (30 minutes), the deposition of mesas on the surface of monocrystalline p-Si was accelerated in the presence of metal ions (Zn) compared to the metal-ion-free environment.

In a metal ion-free environment, the BSCd particles obtained exhibited an oval or spherical shape and were distributed unevenly on the surface. In contrast to the BSCd layers in a metal

environment, where the particles were predominantly distributed in a non-uniform manner, forming primarily hollow structures with a spherical shape. The subsequent increase in anodization voltage (up to 40 V) resulted in minimal changes in the size and shape of the particles. Specifically, the uniform distribution of particles across the surface was the main factor contributing to the formation of spherical-shaped particles.



a) b)

Figure 1. Presents the SEM image (a) and EDS spectrum (b) of the BSCd film obtained on p-Si substrates under an applied bias voltage of 30 V and a current density of 40 mA/cm^2.

The size of the particles could be controlled by varying the magnitude of the anodization current. Increasing the anodization current to 70 mA/cm^2 allowed for an increase in particle size up to 70 nm. Figure 1 illustrates the SEM image (a) and EDS spectrum of the BSCd film obtained on p-Si substrates under an applied bias voltage of 30 V and a current density of 40 mA/cm^2.

After doping, the passivation of Si wafers was carried out under a pressure of 10 Pa for 6 minutes, at a discharge voltage of 600 V and a current density of 1 mA/cm^2.

In the third chapter The dependence of the electrical and photoelectric properties of $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ thin films on their composition, deposition, and thermal treatment regimes

was investigated. The thickness values of the formed thin films within 4, 6, and 8 hours were correspondingly 210, 775, and 1375 nm. The thickness of the films increased linearly with the deposition time. Optical transmission (T%) and absorption (A) spectra of ZnSeTe thin films in the wavelength range of λ = 300-1100 nm showed a correlation between the optical transmission and film thickness. Furthermore, it was found that the absorption edge of the thin films in the range of 300-330 nm was shifted to approximately 310, 320, and 330 nm for the respective deposition intervals of 4, 6, and 8 hours. The increase in film thickness with deposition time resulted in an increase in the absorption coefficient. The dielectric constants of various films were calculated, and it was determined that the deposition interval widened with increasing film thickness, leading to an increase in the true dielectric permittivity of the thin films, which can be expected to enhance their performance.

The morphology and crystallographic properties of $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ thin films were studied as a function of technological and thermal treatment regimes. The thickness of the investigated thin films was examined using an IR-14-type interferometer and an NT-MDT-type electron microscope. The spectral distribution of the experimental optical transmission measurements of $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ thin films before and after thermal treatment at 360°C for 10 minutes in air, oxygen, and argon environments were analyzed. Prior to thermal treatment, during thermal treatment at 360°C for 10 minutes in air, oxygen, and argon environments, and after thermal treatment, the spectral distribution of the experimental optical transmission measurements of the thin films was described. The interpretation of the optical transmission spectra of S-Se and S-Te based thin films in the visible range is challenging due to their complex structures. In contrast, the intensity of oscillations in Te-based thin films is less pronounced, indicating their more homogeneous nature and lower concentration of metal-semiconductor residual states. The complex structure of the S-Se and S-Te based thin films can be attributed to incomplete crystallization of the films

during deposition, possibly due to the absence of synchronous ion exchange, and the presence of vacancies in the film. Such non-homogeneities and incomplete connections on the surface lead to easy absorption of oxygen, resulting in the formation of various chemical and compositional metal oxides during thermal treatment in air. As a result, the short-wavelength region of the optical transmission spectrum shifts due to the formation of metal oxides. This shift is more pronounced in an oxygen environment during thermal treatment. The increase in film non-homogeneity reduces the intensity of the maxima associated with metal oxides. In Se-Te-based thin films, only low-intensity regions at short wavelengths were observed during thermal treatment in an argon environment. During thermal treatment in an argon environment, the slope of the portion of the spectral distribution corresponding to the absorption edge increases significantly, indicating complete crystallization. These samples can be used as optical filters with a sharp transmission edge. In the wavelength range up to 1000 nm, the maximum optical transparency of the S-Se based thin films after thermal treatment in an argon environment reaches approximately 90%. In general, the optical transparency of $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ thin films varies between 44% and 90% for transparent samples. The relatively high values of the optical transmission indicate their potential use in solar energy conversion devices. The forbidden bandgap width (Eg) of the thin films was calculated by extrapolating the dependence of $(\alpha \cdot h\nu)^2$-n on photon energy using the method of extrapolation. These dependences follow the linear relationship at the absorption edge, indicating the true crystalline structure of the investigated compositions of the thin films.

In Figure 2, the lnα versus hν dependence has been established for the investigated thin films. Using the Vegard's law approach, the forbidden bandgap width values of the various composition $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ thin films were calculated and compared with the values obtained from optical measurements. The forbidden bandgap width of the thin films follows Vegard's law, and the calculated values based on the expression are almost in

agreement with the values obtained from optical measurements with an accuracy of approximately 0.02%.

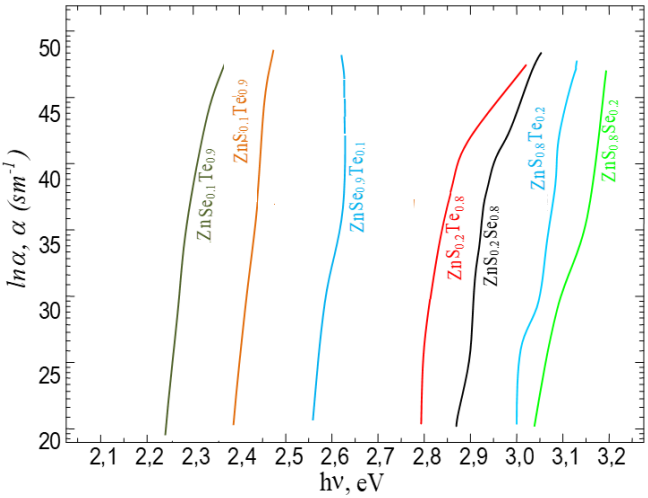


Figure 2. Urbach exponential tail for various composition $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ thin films.

In this chapter, the photokinetic properties of $A^{II}B^{VI}$ compound semiconductor thin films were examined, as well as their deposition and thermal annealing technological regimes, depending on the anion and cation substitution. During the investigation of $ZnS_{1-x}Se_x$ ($0.45<x<0.6$) thin films, photostimulated processes causing changes in photosensitivity were discovered. It was found that $ZnS_{1-x}Se_x$ thin films, when continuously illuminated with visible light and slowly cooled from 350 to 400 K down to 80 K, exhibit a photocurrent observed at 80 K in the dark that is approximately 80 to 100 times higher than the steady-state photocurrent of the samples cooled in the dark.

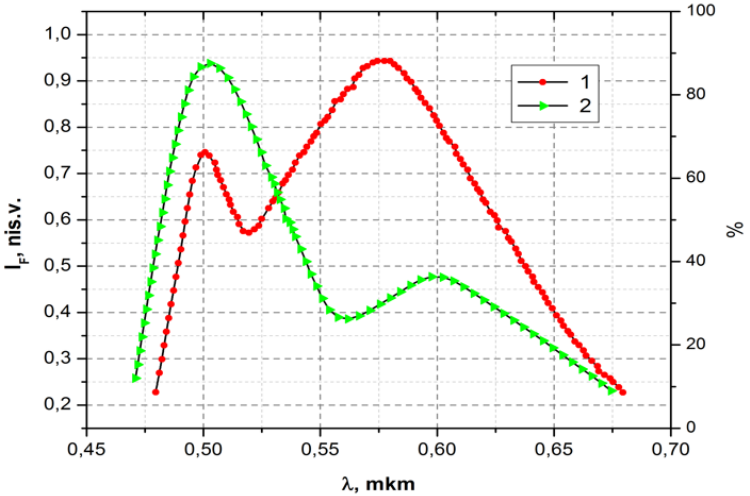


Figure 3. Present the spectral distribution of photocurrent in $ZnS_{1-x}Se_x$ thin films at 80 K: 1 - after cooling from 300 K in the dark; 2 - during illumination with visible light.

FKR sensitization of $ZnS_{1-x}Se_x$ (x=0.2) thin films was observed within 10 to 15 minutes in air after TE, with an activation energy of 0.15 to 0.18 eV. The spectral distribution of photocurrent for unsensitized (curve 1) and sensitized (curve 2) thin films is shown in Figure 2. For $ZnS_{1-x}Se_x$ films with x = 0.2 and 0.8, the depths of the respective photoresponse peaks were determined to be 1.57 and 1.38 eV, according to the long-wavelength boundaries of the conduction band determined by additional photoresponsivity peaks. After 3-7 minutes of TE at 380-400 K, the photosensitivity of the studied films increases significantly. The photoresponsivity spectrum of the investigated films widens towards longer wavelengths after TE and an additional maximum is clearly observed at λ_2 = 0.95-1.19 μm. As the annealing time increases ($3 \leq \tau \leq 7$ min), the intensity of the first maximum decreases, while the intensity of the second maximum increases. After 7 minutes of thermal annealing, the first maximum disappears, while the intensity of the second maximum reaches its maximum value. The presence of an

additional maximum in the photoresponsivity spectrum of $ZnS_{1-x}Se_x$ thin films at λ_2 = 0.95-1.19 μm, observed by us, indicates the introduction of new photoactive centers due to the dissociation of donor-acceptor pairs in the studied films.

In the fourth chapter, CdS, $ZnS_{1-x}Se_x$, and $ZnSe_{1-x}Te_x$ based heterostructures were investigated. The electrical and photoelectric properties of Si-CdS heterojunctions were studied depending on the size of the crystals and specimens. The investigated heterojunction's steady-state I-V characteristic revealed its rectifying properties. The rectification factor increased from 7.4 to 10 nm as the size of the specimens increased from 180 to 1100. Further increase in specimen size led to a sharp decrease in rectification (~12÷15). The photo and gas sensitivity of the heterojunction was investigated depending on the size of the crystals and specimens. For heterojunctions with a size of 7.4 nm, the direct conductivity at U=1 V was observed, and for heterojunctions with sizes of 10 and 30 nm, it was studied depending on the concentration of various gases (oxygen, nitrogen, methane, and ethanol vapor). Direct conductivity was measured in different concentrations of air at U=1 V. For heterojunctions with a size of 10 nm, the direct conductivity remained unchanged, while for heterojunctions with a size of 30 nm, it decreased with increasing air concentration.

During the study, monocrystalline p-Si <100> wafers with a thickness of 800 μm and a specific resistance of (0.8-1) Ω·cm were used as substrates. The investigated p-Si/$ZnS_{1-x}Se_x$ heterojunctions were prepared by electrochemical deposition of 520-530 nm thick $ZnS_{1-x}Se_x$ (x=0, 0.1, 0.2) thin films on p-Si wafers, which were grafted in various concentrations of KOH+ C_3H_8O and HF+HNO_3 solutions. The electrical properties of the heterojunctions were investigated depending on the duration of grafting in KOH+ C_3H_8O and HF+HNO_3 solutions, the temperature of the solution, and the concentration of additives in the solution (KOH and HF (1-5 wt%); Ethanol and HNO_3 (3-10 vol%)).

Table 1.

Si wafers in KOH+C_3H_8O solution Development Modes

Example	*KOH* k.wt%	*C_3H_8O* k. vol%	M. k. ^{0}C	Inoculation.m., min.
SK1	1	3	80	20
SK2	1	3	80	30
SK3	2	6	80	30
SK4	3	6	80	40
SK5	3	10	90	50
SK6	5	10	80	60
Note: number-examples; concentration of KOH to.-KOH; C_3H_8O k.-concentration of C_3H_8O; M.к. - solution concentration at 0C; Ash.m.-vaccination period				

In the KOH + C_3H_8O (samples in Table 1) and HF+HNO_3 (samples in Table 2) etching process on silicon, the presence of pyramids (or pits) on the surface is induced, and their morphology and size depend on the temperature, concentration, and etching duration of the process.

The formation of pyramids on the surface becomes visible after 20-30 minutes of etching (SK1, SK2, SK3, SH1, SH2, and SH3 samples). Therefore, in this phase of the dissertation work, heterojunctions based on silicon (Si) etched for ≥ 20 minutes were investigated. It has been found that etching within 20-30 minutes leads to the formation of unevenly distributed pyramids on the Si surface. It has been determined that controlling the concentration of the etchant is necessary to achieve the desired distribution of pits and pyramids.

Another important finding was made after 40 minutes of etching. Specifically, during this period, the Si surface (sample SK4 and SH4) is covered with relatively evenly distributed pyramids (or pits), which is considered crucial for enhancing the stability of solar cell parameters (Table 1 and Table 2).

Table 2.

Silicon wafers in $HF+HNO_3$ solution vaccination schedules

Example	HF k. wt, %	HNO_3 k vol,%	M. k. ^0C	Inoculation.m., min.
SH1	1	3	80	20
SH2	2	3	80	30
SH3	3	6	80	30
SH4	5	8	80	40
SH5	6	9	90	50
SH6	5	10	80	60
Note: Num.-examples; HF k. HF concentration; HNO_3 k.- HNO_3 concentration; M.k. - concentration of the solution at 0C; Ash.m.-vaccination period				

Moreover, no other changes have been observed in the morphology of the silicon surfaces for the subsequent increments of concentration, duration, and temperature (samples SK5, SK6, SH5, and SH6).

All types of heterojunctions exhibit rectification characteristics specific to diodes, and the rectification direction is consistent with the positive direction of external bias in p-Si. Despite the relatively close lattice parameters of p-Si and n-ZnS semiconductor materials (corresponding to 5.431 Å and 5.410 Å, respectively), the high specific resistivity of ZnS buffer layers prevents achieving good rectification in heterojunctions based on undoped p-Si (k=50-80).

On the other hand, the presence of an oxide layer of SiO_x type on the surface of silicon, which is practically impossible to eliminate using various technological methods (the thickness of this layer can reach up to 50-200 Å at room temperature), is one of the reasons for poor rectification. However, in the proposed methodology, with the slight doping effect of $KOH+C_3H_8O$ solution, not only the undesirable oxide layer on the surface is removed, but also the formation of various types of nano- or micro-heterojunctions in the transition region has been achieved.

As a result, all parameters of the final matrix are determined by the parameters of these small-scale heterojunctions.

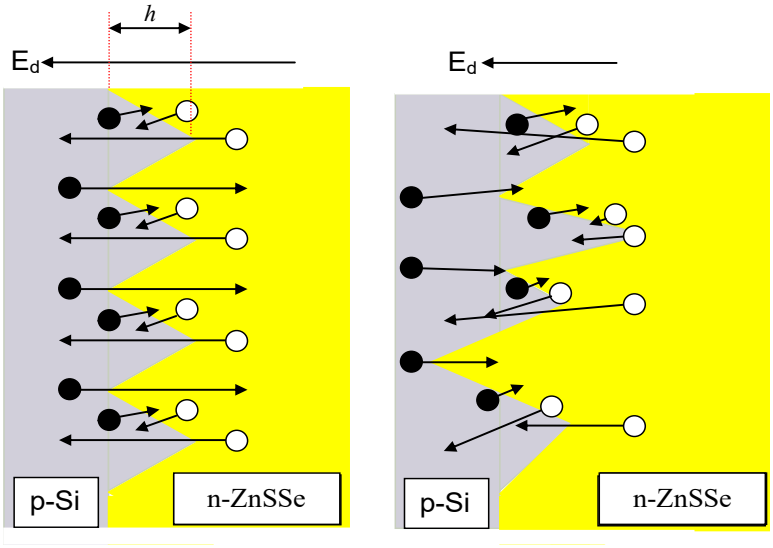


Figure 4. Pyramidal and oval textured heterojunctions schematic representation of the transition zone

In p-Si/ZnS heterojunctions, thermionic emission mechanism predominates in the current transport. For un-doped p-Si/ZnS heterojunctions, the non-ideality factor (A) of the diode ideality factor (VAX) is 2.4 (U = 0.5-0.88 V) and 4.3 (U ≥ 0.89 V). The relatively large non-ideality factor of VAX is actually attributed to the significant resistance of the ZnS delicate layers and the presence of SiO_2 (or SiO-type oxide layer) on the surface of Si, contrary to what is claimed. If the series resistance were significantly small and there were no oxide layer, VAX would obey only the exponential law in the forward direction, and A would be equal to 1. Due to small external voltages, most of the voltage drops across the junction, hence VAX exhibits exponential dependence (A ≈ 1).

Table 3.
Electrical parameters of p-Si/ZnS$_{1-x}$Se$_x$ heterojunctions

Examples	k (correction factor)	R, (Om·sm to resistivity)	A (imperfection factor)
Unvaccinated *p-Si/ZnS*	90	2200	2.4 və 4.3
p-Si/SK1/ZnS	180	700	2.0
p-Si/SK2/ZnS	280	340	2.0
p-Si/SK4/ZnS	600	95	1.58
p-Si/SK4/ZnS$_{0.9}$Se$_{0.1}$	1790	16	1.4
p-Si/SK4/ZnS$_{0.8}$Se$_{0.2}$	1200	64	1.6
p-Si/SH1/ZnS	100	950	2.7
p-Si/SH2/ZnS	190	670	2.6
p-Si/SH4/ZnS	480	210	2.0
p-Si/SH4/ZnS$_{0.9}$Se$_{0.1}$	1400	48	1.7
p-Si/SH4/ZnS$_{0.8}$Se$_{0.2}$	900	124	1.9

With the increase of external stress, the applied stress decreases sequentially, and at the same time, the trapping of free carriers occurs in the oxide layer. This leads to an increase in the non-ideality factor of VAX due to the increased recombination processes in the depletion region.

Despite the lack of significant reduction in the specific resistance of ZnS delicate layers due to etching, heterodiodes based on them do not exhibit significant improvement in rectification. Therefore, in the dissertation work, the delicate layers of ZnS-ZnSe and ZeSe-ZnTe systems were used. The addition of a small amount of Se (20%) to ZnS has allowed increasing the value of rectification coefficient k up to 1800-2000.

In fact, increasing the amount of Se would have reduced the specific resistance of the delicate layers of the ZnS-ZnSe system and thus improved the rectification of the heterojunctions. However, increasing the molar amount of Se up to x=0.2 leads to an increase

in the mismatch between the lattice parameters of Si and $ZnS_{1-x}Se_x$ and consequently an increase in the concentration of defects in the transition region. This leads to a deterioration of the parameters of heterojunctions based on them.

Table 4.

Electrical parameters of p-Si/$ZnSe_{1-x}Te_x$ heterojunctions

Examples	k (correction factor)	R, (Om·sm to resistivity)	A (imperfection factor)
Unvaccinated *p-Si/$ZnSe_{0.8}Te_{0.2}$* before TO	25	1700	2.5
Unvaccinated *p-Si/$ZnSe_{0.8}Te_{0.2}$* after TO	1280	140	1.8-2.0
p-Si/SK2/$ZnSe_{0.8}Te_{0.2}$	1600	80	1.5
p-Si/SK4/$ZnSe_{0.8}Te_{0.2}$	2500	34	1.2
p-Si/SH4/$ZnSe_{0.8}Te_{0.2}$	2200	60	1.2

The electrical and photoelectric properties of Si-CdS heterojunctions were investigated depending on the size of crystallites and grains. It has been determined that the value of the rectification coefficient (K) determined at U = 1 V and the current conduction mechanism depend on the sizes of grains and crystallites.

The rectification direction on c-Si corresponds to the positive polarity of the external bias. As seen from the I-V characteristic, an increase in the size of grains from 8-11 nm to 10-16 nm leads to an increase in rectification from 82 to 1100 at U = 1 V. Further increase in the size of grains causes a sharp decrease in the rectification coefficient (K = 30-40). The size of CdS crystallites deposited on c-Si/PS at a potential of 0.82 V (with grain sizes of 7.4, 10, and 30 nm) can be controlled by choosing the size of silicon grains.

CdS layers show nanoscale texturing by increasing the size of grains from 10 to 30 nm. Depending on the size of crystallites and grains, the photo and gas sensitivity of heterojunctions were investigated. It has been determined that the values of the rectification coefficient and the current conduction mechanism depend on the sizes of grains and crystallites. The direction of the junction in c-Si layers corresponds to the combination of positive polarity of the external bias. The rectification coefficient increases from 180 to 1100 by increasing the size of grains from 7.4 to 10 nm. Further increase in the size of grains leads to a sharp decrease in rectification (~12-15).

It has been determined that the degree of adsorption depends on the size of grains. To confirm this fact, heterojunctions were heated in vacuum at 50-70°C and J-V characteristics were obtained in vacuum. It has been determined that in heterojunctions with grain sizes of 7.4 and 10 nm, rectification remains virtually unchanged.

In general, the direction of rectification VAX in heterojunctions taken at various values of the deposition potential.

$$U_a = I_0 e^{-\frac{eU}{AkT}} \tag{1}$$

The statement can be described by an exponential law. Here, Is represents the reverse saturation current, e is the charge of an electron, U is the applied external voltage, $k = 8.7 \times 10^{-5}$ eV/K is the Boltzmann constant, T is the absolute temperature, and A is the non-ideality factor of the diode.

It has been determined that the dependence of the ideality factor of heterojunctions on the composition of the thin layers is non-monotonic.

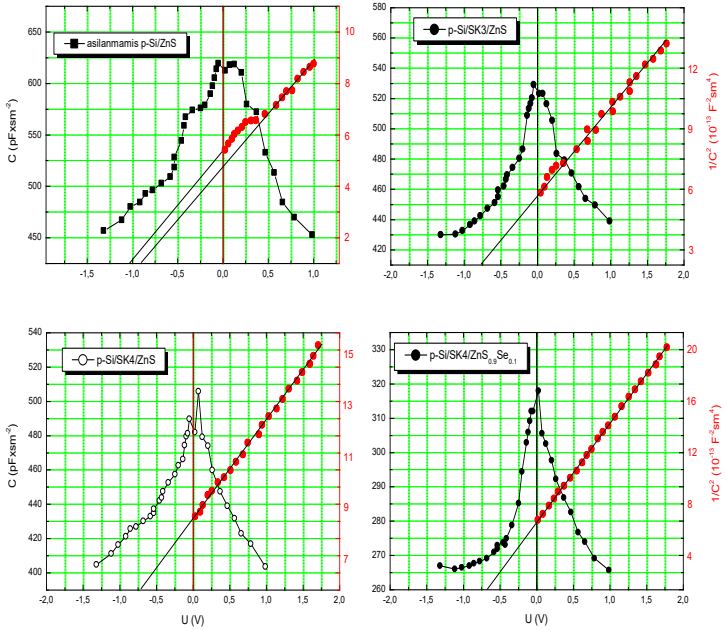


Figure 5. VFX of p-Si/SK/$ZnS_{1-x}Se_x$ heterojunctions based on grafted SK substrates in various modes at a frequency f = 60 kHz at room temperature.

On the other hand, the dependence of the specific electrical resistance on the composition of the $ZnSe_{1-x}Te_x$ thin films is also non-monotonic. This effect is also manifested in the dependence of the series resistance (Rs) of heterojunctions on the composition of the layers. In heterojunctions, the series resistance was calculated by the approximation of the linear part of the dependence dU/dI = f(U) at the straight section of the lnI = f(U) dependence. In heterojunctions with $x \neq 0.6$, the lnI = f(U) dependencies consist of two sections, and the slopes of the linear sections are sharply dependent on temperature. The presence of two sections in the graphs confirms the presence of discrepancies in the doping parameters and the presence of metal hydroxides remaining on the surface and volume of the layers during the deposition process. In heterojunctions with x=0.6, only one section with a slope is observed

in the lnI = f(U) dependence graphs. The compatibility of the doping parameters of $ZnSe_{1-x}Te_x$ and p-Si leads to the disappearance of the second section observed in other compositions. The concentration of surface states related to the incompatibility of the doping parameters was calculated and found to be Nd ≈ 6×1013 sm^{-3}. Additionally, the weak slope of the lnI = f(U) dependence graphs in heterojunctions with x=0.6 indicates the dominance of multi-step tunnel-recombination emission currents in them. Despite the minimum number of defects in heterojunctions with x=0.6 due to the compensation of the incompatibility of the doping parameters, the relatively large value of the non-ideality factor (n=1.7) indicates a sufficient concentration of reaction products and defects related to oxygen in the transition region. The space charge region in heterojunctions is also determined by the concentration of defects. Volt-farad characteristics of heterojunctions with x≠0.6 in the C^{-2} = f(U) measurement are composed of several linear sections, relatively obeying Ohm's law. The value of the electric conductivity in such heterojunctions depends on the external field intensity and the values of the contact potentials (Vc) obtained from VAX and VFX differ from each other. However, volt-farad characteristics in heterojunctions follow a linear law in the C^{-2} = f(U) measurement and the value of electric conductivity is weakly dependent on the others but relatively small. The linear law observed in VFX in the C^{-2} = f(U) measurement indicates a sharpness in the border of the transition region. The observed relative deviations in VFX, despite the resolution of the incompatibility of the doping parameters, indicate the presence of remaining metal hydroxides. In the dissertation work, the energy depth and nature of defects in the transition region were determined using the capacitance-voltage spectroscopy. Among the capacitance spectroscopy methods in the transition region, the capacitance-voltage-temperature spectroscopy methods are more widely applied and allow for a more accurate diagnosis of the transition region. In the presence of oxygen, the height of the observed narrowing peaks in the characteristic decreases due to the emptying of both levels, and the existence of pillars is virtually absent in heterojunctions with x=0.6. From this, it can be concluded that the recombination centers formed during the technological process

and subsequent entry of oxygen into the surface can be controlled, i.e. their concentration and activation energy can be controlled by selecting the composition and thermal treatment regime of the layers. In heterojunctions based on p-Si/$ZnSe_{1-x}Te_x$ thin films, the photoresponse is determined not only by the cathode potential but also by the thickness of the layer. One of the methods applied to reduce the series resistance in heterojunctions is to minimize the thickness of the buffer layer in contact, taking into account the optical laws as much as possible. However, considering that the degree of light absorption in the layer is non-monotonically dependent on the thickness of the layer, it can be concluded that for the overall improvement of efficiency, not only electrical but also optical properties must be taken into account. Therefore, for achieving maximum efficiency, a specific thickness should be chosen based on a specific material. All heterojunctions prepared at the optimal value of the deposition potential demonstrate photovoltaic effect immediately after deposition, and the sign of the photovoltage does not change in the entire photoresponse range. Similar to the electrical parameters, the maximum photoelectric parameters were obtained in heterojunctions based on delicate layers with x=0.6.

After thermal treatment under optimal conditions in an oxygen environment (at a temperature of 600°C for 15 minutes), the reconstruction of the transition region in heterojunctions and the electron-molecular processes occurring on the surface and in the volume of delicate layers (such as recrystallization, dissociation of metal hydroxides, desorption of oxygen, etc.) result in the reformulation of the transition region, causing variations in the short-circuit current (Jsc) and open-circuit voltage (Voc) to a noticeable extent. At the same time, the photoelectric parameters, like the electrical parameters of the heterojunctions, improve only under specific conditions of thermal treatment. It should be noted that over a period of 5 years, the heterojunctions exhibit a maximum degradation of only 0.01%, which allows them to be utilized as stable and, most importantly, environmentally friendly photoconverters.

CONCLUSION

1. Optimal composition has been determined to ensure the high sensitivity of $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ nanostructured layers, and the deposition technology and thermal annealing process regimes have been identified.

2. The forbidden bandgap (Eg) of $ZnS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ thin films with different compositions has been calculated. These bandgaps follow the linear law at the edge of the bandgap, indicating the direct bandgap nature of all investigated compositions of thin films.

3. The observed photochemical reaction in $ZnS_{1-x}Se_x$ thin films is related to the formation and decomposition of donor-acceptor complexes, which are determined by the concentration of the film and the TE condition.

4. As a result of the grafting in KOH + C_3H_8O and HF+HNO_3 solutions, the surface recombination velocity for p-Si/ZnS1-xSex and p-Si/$ZnSe_{1-x}Te_x$ heterojunctions is properly reduced to k=1800 and k=2500, respectively.

5. It has been determined that the key properties of electrochemically obtained p-Si/$ZnS_{1-x}Se_x$ and p-Si/$ZnSe_{1-x}Te_x$ heterojunctions are influenced by the presence of generation-recombination processes in the absorber layer, and the volt-farad characteristics indicate the sharp anisotropic nature of this heterojunction structure.

6. The current transport mechanism in p-Si/$ZnS_{1-x}Se_x$ and p-Si/$ZnSe_{1-x}Te_x$ heterojunctions has been converted from thermoelectronic to generation-recombination mechanism due to thermal annealing.

7. The utilization of wide bandgap amorphous ZnS layer as a buffer layer in Glass/ITO/ZnS/ZnTe/CdTe/CdS structure significantly improves all parameters of these structures as solar cells, and indicates the superiority and suitability of multi-layered structures compared to two-layered ITO/ZnTe/CdTe/CdS structures.

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Candidate's personal contribution:

[8], [10], [12], [13], [14] - independently conducted the works;
[1], [2], [3], [6], [9], [11] - participated in problem formulation, conducting research, and generalization of results in the works;
[4], [5], [7] - participated in report preparation, result analysis, conducting laboratory tests, and generalization of results in the works.
[4], [8], [10], [12], [13], [14] - performed independently.

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