UDC: 621.315.592; 541.65

IMPACT OF IONIZING RADIATION ON PHYSICAL PROPERTIES OF II-IV GROUP CHALCOGENIDES, DEFECT FORMATION ENERGY

M.A. Mehrabova
Institute of Radiation Problems of ANAS
m.mehrabova@science.az

Abstract: Density Functional Theory is used for ab initio calculations of band structure for ideal and defective semiconductors Cd(Pb)Te and $Cd(Pb)_{1-x}Mn_xTe$ in Atomistix Toolkit program and also Bond Orbital and LCAO methods are used for calculations for GaS, GaSe, InSe. The density of states, band gap, total energy, magnetic moments, and number of electrons, Fermi level, defect formation energies and threshold energies are determined.

The optimum conditions for obtaining perfect Cd(Pb)Te and $Cd(Pb)_{1-x}Mn_xTe$ epitaxial films, and structures on their base are determined. Changes in the crystal structure, surface morphology, VAC, photoconductivity and optical parameters after irradiation of epitaxial films $Cd_{1-x}Mn_xTe$ by γ-quanta of doses $D\gamma \leq 25$ kGy and epitaxial films $Pb_{1-x}Mn_xTe$ by electron fluxes $\Phi \leq 7 \cdot 10^{17} cm^{-2}$ have been established. The possibilities of creation of photosensitive heterojunctions based on n-CdTe/*p*-Cd1-xMnxTe (x=0.4) and *n*-$Pb_{1-x}Mn_xTe$/*p*-$PbTe_{1-x}Se_x$ epitaxial films are determined.

Keywords: Ab initio, DFT, Bond Orbital method, LCAO, chalcogenides, electronic structure, defect formation energy, epitaxy, irradiation, photoconductivity, absorption

1. Introduction

II-IV group chalcogenides have been successfully applied in microelectronics, optoelectronics and spintronics. A number of instruments, including solar cells, radiation detectors, IR detectors, photodetectors, optical isolators, etc. were created on the basis of these semiconductors [1-6]. Obtain of radiation-resistant and radiation-sensitive materials with stable electrical and optical characteristics is one of the actual issues of modern physics. An important task is the study of defect formation mechanism of II-IV group chalcogenides, their epitaxial films, structures based on them and determination of the effect of ionizing radiation on physical properties. It should be noted that, in the literature there are papers [7-11] devoted to the study of the processes of radiation defect formation (RDF) in bulk crystals. However, there are no unique models for formation, mechanism and evolution of RDF in chalcogenides, their epitaxial films and structures based on them.

In this paper, it has been carried out ab initio calculations of band structure (BS) of ideal and defective semiconductors Cd(Pb)Te and $Cd(Pb)_{1-x}Mn_xTe$ by the method of Density Functional Theory (DFT) in Atomistix ToolKit program, as well as GaS, GaSe, InSe by Bond Orbital and LCAO methods and determined density of states (DOS), band gap, total energy, magnetic moments (MM), number of electrons, Fermi level, also defect formation energy (DFE), threshold energy. The results of the conducted experimental works are presented which had good accord with the theoretical results.

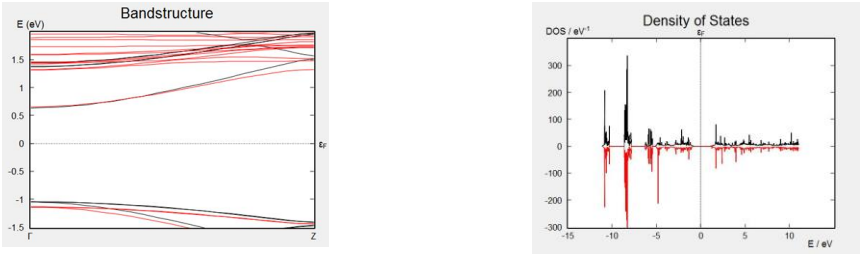
2. Theoretical part

Relaxation and optimization processes of atomic structure have been carried out for ab initio calculations of band structure of ideal and defective semiconductors Cd(Pb)Te and

$Cd(Pb)_{1-x}Mn_xTe$ by DFT. For comparative analyses, calculations were first carried out for CdTe of 8 and 64 atoms. From analyses of partial densities of electron states of the films (PDOS) it was established that the upper levels of valence band which are located in the region [-5; 0] eV, mainly occur from 5*p*-state of Te atoms, but the lower levels of conduction band which are located in the region [5; 0] mainly occur from 5*s*-state of Cd atoms. The calculated value of band gap width was E_g=1,53 eV in FFT algorithm, E_g=1,64eV in Multigrid algorithm. The total energy of supercell Cd32Te32 was E_t=-68285.96 eV.

Further calculations were carried out for the defective (vacancy, interstitial atom, Frenkel pair) supercells Cd32Te32. It is established that defects in semiconductors lead to formation of MM, band gap width changes, local levels are formed in the forbidden band.

BS, DOS, MM, number of valence electrons have been calculated for supercells Cd30Mn2Te32 and its defect states in both ferromagnetic (FM) and antiferromagnetic (AFM) phases. A crystal cell of 16, 64, 96, etc. atom has been examined. It has been revealed that, DS of supercell Cd30Mn2Te32 consists of 3 parts in the valence band: 1) the upper part of the valence band is mainly formed from *p*-states of Te atoms with a certain contribution of s-states of Cd atoms of the lower levels of the upper parts of the valence band, 2) the middle part has been formed from *d*-states of Mn atoms and *s*-states of Cd atoms which are located below the maximum of the valence band 7eV, 3) the main peak at 10eV below the maximum of the valence band has been formed mainly from *s*-states of Te atoms. The lower part – bottom of the conduction band is formed from *s*-states of Cd atoms and *p*-states of Te atoms. The peak at ~ 2eV above the minimum of the conduction band is formed mainly from *d*-states of Mn atoms (fig.1).



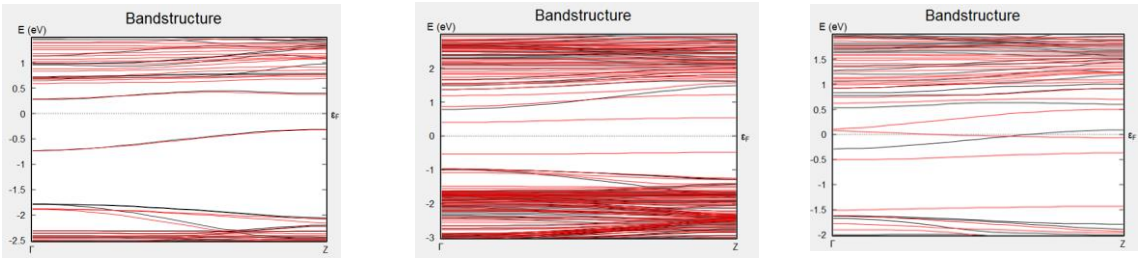
a) *b)*

Fig.1. Cd30Mn2Te32, FM. Calculated band gap width E_g=1.62eV, $E_{c\uparrow}$=0.61eV, $E_{v\uparrow}$=-1.01eV a) band structure, c) density of state

The band gap has been calculated for $Cd_{1-x}Mn_xTe$, which is E_g=1.73eV (x=0.06), E_g=1.68eV (x=0.03), E_g=1.65eV (x=0.02) and coincides with our experimental data. It is determined that the band gap width increases linearly with an increase in the amount of Mn, but there occurs an insignificant decrease in the lattice parameter with Mn increasing.

The presence of Mn atoms in the composition of $Cd_{1-x}Mn_xTe$ leads to the formation of MM which equals μ=5.113μ_B.. Comparison of total energies for FM and AFM shows that the AFM phase is more stable. The accuracy of the calculations was 0.001μ_B. The total sum of electrons was 556.

Ab initio calculations of BS have been carried out for defective supercells Cd30Mn2Te32 (fig.2). It has been established that the defects in $Cd_{1-x}Mn_xTe$ lead to the following changes: the band gap width increases, deep levels appear, Fermi level shifts towards the valence or conduction band (conductivity inversion) in the forbidden band, magnetic moments appear near the defects, transition occurs from FM to AFM phase and back [12,13].



a) *b)* *c)*

Fig.2. Band structure of supercells Cd30Mn2Te32 in FM phase a) V_{Te}, b) I_{Te} c) FP_{Te}

The defect formation energies (DFE), defects for $Cd_{1-x}Mn_xTe$ with supercells of 32-, 64-, 96-, 128-, 256 - and 512 atoms have been calculated in the paper. DFEs were determined for various charge states for Te and Cd vacancies, interstitial Te and Cd atom, and also for Frenkel pair. DFE was determined for different supercells for various charge states by extrapolation method, for example, for V_{Te} it was found to be 6.4eV (fig.3). Threshold energies of defect formation have been determined, for V_{Te} it was 467keV [14].

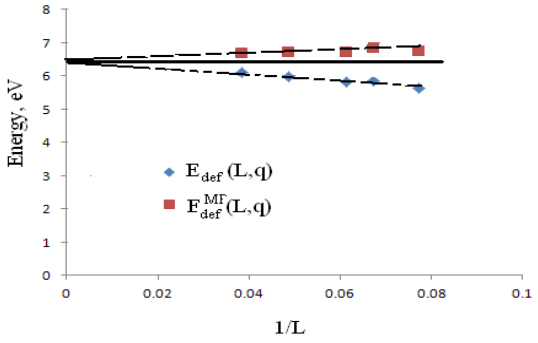


Fig.3. $E_{def}(L,q)$ for V_{Te} for supercells of 32, 64, 96, 128, 256 and 512 atoms (blue diamonds) and calculated energies by the scheme Makov-Payne $E_{def}^{MP}(L,q)$ (red squares) for charge state q=2

BS and DOS calculations for $Pb_{1-x}Mn_xTe$ (x=0.06) were carried out for AFM and FM phases on a 2×2×2 grid of κ- points in the Brillouin zone including G point. The calculated value of the band gap width for $Pb_{1-x}Mn_xTe$ (x=0.06) was E_g= 0.43 eV and the total energy E_t=-38799.7 eV in the FM phase, and E_g= 0.55 eV, E_t=-38799.7 eV in the AFM phase. PDOS analysis revealed that the lower part – bottom of the conduction band is mainly formed by 6*p*- Pb orbital and 3*d*- Mn orbital, and the maximum – upper part of the valence band by 5*p*- Te orbital and 3*d*- Te orbital with some contribution of 6*p*- Pb orbitals. In addition, the upper part of the conduction band which is located at ~5eV above the minimum of the conduction band, is formed mainly from 4*s* and 5*p* Mn atom orbitals and 5*p* Te orbitals. The lower part of the valence band which is ~7eV below the maximum of the valence band, was formed mainly from 6*s*-Pb atom orbitals. Band extremes are located at the same point of *k*-space, at Γ point of the Brillouin zone. They degenerate only on the back and almost mirror each other. The data obtained are in good agreement with the literature data.

On the basis of the calculated values for supercells we can come to the conclusion that, the band gap width decreases and the lattice parameter increases insignificantly in AFM phase with a decrease in Mn concentration in the composition of SMS $Pb_{1-x}Mn_xTe$ which is confirmed

by our experimental results and literary data. In FM phase, the band gap width increases with a decrease in Mn concentration.

BS, DFE and threshold energy of $Pb_{1-x}Mn_xTe$ have been calculated from the first principles of defective supercells Pb30Mn2Te32, for example DFE for Frenkel pair was E_d= 2.81eV, threshold energy was E_t =146 keV.

On the basis of the obtained results it has been revealed that, the defects (vacancy, interstitial atom, Frenkel pair) in $Pb_{1-x}Mn_xTe$ lead to an increase in the band gap width, formation of local levels in the bahnd gap, displacement of Fermi level, formation of MM near defects, transition from FM to AFM phase and back.

The band structure of defective and doped A^3B^6 semiconductors (GaS, GaSe, InSe) has been determined in the work. Energies of local levels from defects – vacancies and their compensated states formed in the forbidden band and in the valence band in A^3B^6 semiconductors have been calculated. Calculations for GaS, GaSe, InSe semiconductors with anion and cation vacancies and with impurity have been carried out on the basis of the theory of Green's function, Bond Orbital and LCAO methods. Mechanism of defect formation and restoration of initial properties of defective semiconductors has been established. It is determined that within the compensation of vacancies by atoms of the same subgroup with the same tetrahedral coordination, the ionic radius of which is smaller than the ionic radius of the substituted atom, for example, when the cation vacancy is replaced by Tl atom, the local levels formed from vacancy completely disappear. Thus, the cations with a small ionic radius and tetrahedral coordination, replaced in defective semiconductors, restore the crystal parameters. Atoms with different coordination and large ionic radius create additional defects and local levels. Localized levels from vacancies do not disappear completely. Using this mechanism, it is possible not only to restore the previous parameters of the crystal, but also to improve its characteristics [15-19].

It has been studied the accumulation of charge carrier in the structures of metals - *p*-GaS (GaSe, InSe), theoretically determined the optimal values of the sample thickness, the electric field strength applied to the contacts and photon energies of the incident light at which the structure can work efficiently [20].

3. Experimental part

The influence of γ-radiation on electrophysical, optical and photoelectrical properties of SMS $Cd(Pb)_{1-x}Mn_xTe$ (x=0.01-0.07) epitaxial films has been studied depending on thickness of the samples, Mn concentration and γ-irradiation dose.

In order to grow $Cd(Pb)_{1-x}Mn_xTe$ (x=0,01-0,07) epitaxial films it has been used synthesized samples of $Cd(Pb)_{1-x}Mn_xTe$ solid solutions of the corresponding compositions. Crystal structure of the synthesized solid solutions has been studied by *X*-ray diffraction method. The spectra showed that these solid solutions of $Cd_{1-x}Mn_xTe$ crystallize on the lattice of zinc blende of CdTe (cubic, sphalerite) and have parameters a_1=6.4785, a_2=6.4775, a_3= 6.4745. Crystalline perfection of the synthesized solid solutions of $Cd_{1-x}Mn_xTe$ (x=0.01-0.05) was studied by ESR method. It was determined that Mn^{2+} ions were uniformly embedded in the crystal lattice of CdTe compound.

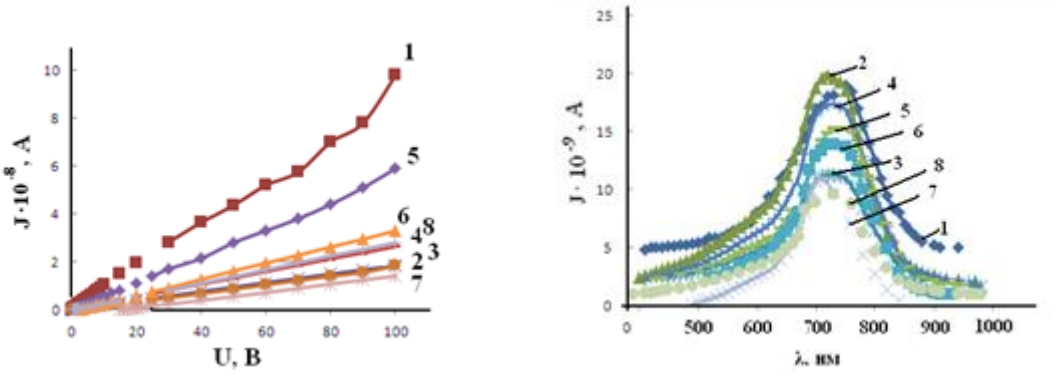
$Cd_{1-x}Mn_xTe$ (x=0.01–0.07) epitaxial films were obtained on glass and mica substrates by of Molecular Beam Condensation (MBC) method in the vacuum evaporation plant УВН-71-П3 with steam-oil pumping and nitrogen trap at working pressure of residual gas $(1\div2)10^{-4}$Pa. By using additional source of Te vapor and controlling temperature, it has been determined the optimum conditions (T_{sou}=1000–1100K, T_{sub}=570–670K) for obtaining $Cd_{1-x}Mn_xTe$ (x=0,01-

0,07) epitaxial films with a perfect structure and clean, smooth surface, without inclusion of the second phase.

The crystal structure of the films was studied by electron diffraction, electron microscopy and *X*-ray diffraction methods [21, 22]. The thisckness of the obtained films was controlled with a metallographic microscope МИИ-4. It has been established that $Cd_{1-x}Mn_xTe$ epitaxial films grow on glass and mica substrates with the plane (111) of the cubic face-centered lattice with the parameter a=6.481Å. It is determined that the obtained films of $Cd_{1-x}Mn_xTe$ have an amorphous structure on glass substrates, and polycrystalline on mica substrates at the temperature of substrate T_{sub}=300K. Increase in T_{sub} (≥470K) leads to the obtain of polycrystalline films with a cubic structure (a=6,481Å) on glass substrates, and above 570 K there begins an epitaxial growth on both substrates.

The influence of γ-radiation (E=1.25MeV) on the structure of thin polycrystalline $Cd_{1-x}Mn_xTe$ films was studied. The studies showed that the effect of the irradiation manifests itself in the diffractograms obtained from these films after irradiation. After irradiation with a dose of D_γ<200Gy and a power of P=21rad/sec, there occurs a change in *X*-ray diffraction spectra, the intensity of the reflections changes, new reflections with a weak intensity appear in certain crystallographic directions which is associated with the changes in the crystal structure after irradiation.

The effect of γ-radiation on the electrophysical, photoelectrical and optical properties of $Cd_{1-x}Mn_xTe$ (x=0.01-0.07) thin films on mica and glass substrates was studied. VAC of the initial and γ-irradiated samples of $Cd_{1-x}Mn_xTe$ (x=0.05,0.07) epitaxial films, with thickness d=1-15μm on mica and glass substrates at T_s=300 K has been studied. In the initial samples of $Cd_{1-x}Mn_xTe$ in VAC there is observed a linear part $J\sim U$ corresponding to Ohm's law and quadratic part $J\sim U^2$ [22]. Further, the samples were irradiated by γ-quanta at doses $D_\gamma \leq 900$Gy. The dependencies are presented in fig.4.



a) *b)*

Fig.4. $Cd_{1-x}Mn_xTe$ (x = 0.07) epitaxial films a) VAC b) photoconductivity at U=4B, $J_t=1.7\cdot10^{-9}$A, d=15μm: 1- D_γ=0, 2-D_γ=100Gy, 3-D_γ=200Gy, 4-D_γ=300Gy, 5-D_γ=400Gy, 6) D_γ=500Gy, 7) D_γ=700Gy, 8) D_γ=900Gy

Analysis of the curves can be carried out within the framework of theory of injection currents in solid solutions with no-activation conductivity. The observed character shows that within the irradiation of $Cd_{1-x}Mn_xTe$ films with small doses D_γ=100Gy, a number of deep levels are formed in the forbidden band in which electrons take part, and it leads to a decrease in conductivity. Further irradiation D_γ =300Gy leads to an increase in the conductivity, resulting in the appearance of an impoverished quadratic region. With a further increase in the irradiation

dose D_γ<900Gy, the value of the current decreases, and trapped quadratic region is again observed, but in the dose D_γ=900Gy the current again increases (fig.4,a).

The effect of γ-radiation on the photoconductivity of $Cd_{1-x}Mn_xTe$, (x=0.05, 0.07) epitaxial films was studied. In the initial samples there is a wide band in the photoconductivity spectrum of $Cd_{1-x}Mn_xTe$ epitaxial films, the spectral range covers the wavelength region λ=400nm-1200nm. The band gap width, calculated from the photoconductivity maxima (λ=720nm), is equal to E_g=1,72eV which corresponds to our theoretical results. The dependencies obtained after irradiation with γ-quanta at $D_\gamma \leq$900Gy are given in (fig.4,b). Such a change in the photoconductivity after irradiation by ionizing rays makes it possible to create ionizing radiation detectors based on these semiconductors [23].

Absorption and transmission spectra of $Cd_{1-x}Mn_xTe$ (x=0.07) epitaxial films on glass substrates have been studied, the film thickness has been d=15μm and 22μm. The spectra have been recorded on UV-Visible SPECORD 210 PLUS spectrophotometer in the wavelength region λ=190-1100nm. It is established that the films absorb the light to the wavelength λ=720nm, afterwards there occurs a sharp decrease in the absorption coefficient [24]. The band gap width of $Cd_{1-x}Mn_xTe$ (x=0.07) epitaxial films was determined as E_g=1.73eV, which corresponds to our theoretical calculations.

The studies of the effect of γ-radiation on the optical properties of CdMnTe (x=0.07) epitaxial films with film thickness d=15μm showed that the edge of the absorption changes, there occurs a change in the band gap width, absorption and reflection coefficients, which can be explained by the appearance of the local levels from the formation of defects in the crystal structure.

It has been studied the possibility of creating photosensitive *p-n* heterojunctions based on *n*-CdTe and *p*-$Cd_{1-x}Mn_xTe$ (x=0.4) epitaxial films. *n*-CdTe/*p*-$Cd_{1-x}Mn_xTe$ (x=0.4) heterojunctions (HJ) were obtained by MBC method in a single technological cycle without breaking the vacuum, using additional compensating Te vapor source in the growth process by depositing thin *p*- $Cd_{1-x}Mn_xTe$ layers of the shown composition of the film thickness d=1.5-2.5μm on *n*-CdTe of the thickness d=0.5-1.2μm. It has been established the optimum conditions for obtaining (condensation rate υ=14-16 A/sec, substrate temperature T_s=640-670 K for *n*-CdTe and υ=18-20Å/sec, T_s=470-520K for *p*-$Cd_{1-x}Mn_xTe$) structurally perfect epitaxial films growing in the plane (111) of the face-centered cubic lattice and for creating heterojunctions based on them, photosensitive in the wavelength range λ=0,6-0,8μm, which can be used as solar cells and photodetectors.

In order to study the current-carrying mechanism in *n*-CdTe/*p*-$Cd_{1-x}Mn_xTe$ HJ, dark VACs were investigated at room temperature. VACs are sharply asymmetric, direct currents exceed reverse ones by 10^3-10^4 times at bias of 1V. The height of the potential barrier is U_d=0.52V.

The study of the spectral distribution of photosensitivity showed that CdTe/$Cd_{1-x}Mn_xTe$ HJ are sensitive in the wavelength region λ=0.6-0.8μm. The photosensitivity band in the short-wavelength region of the spectrum is determined by the light absorption in $Cd_{1-x}Mn_xTe$ (x=0.4), and a sharp decrease in the long-wavelength edge of the spectrum is due to the absorption in CdTe.

Structurally perfect epitaxial films of $Pb_{1-x}Mn_xTe$ (x=0.01-0.06) were grown on BaF_2 substrates by MBC method in УВН-71-П3 unit with steam-oil pumping and nitrogen trap at operating pressure of residual gases $(1\div2)10^{-4}$ Pa at substrate temperature T_s=663÷693K. It is established that at the temperature of substrate T_s=663÷673K, temperature of additional Te source T_{Te}=420÷430K and at condensation rates $\upsilon_к$=8÷10Å/s we can obtain epitaxial films of p-type conductivity of thickness 0,5÷1μm, grown in plane (111) parallel to the substrate.

It has been established that at substrate temperature T_s=663÷673K, temperature of additional Te source T_{Te}=420÷430K and at condensation rates υ_c=8÷10Å/s we can obtain epitaxial films of *p*-type conductivity with thickness 0,5÷1μm, grown in plane (111) parallel to the substrate. Using the additional compensation Te source, perfect films with a clean smooth surface have been obtained.

Surface morphology of $Pb_{1-x}Mn_xTe$ (x=0.01, x=0.04) epitaxial films has been studied before and after γ-irradiation at dose D_γ=10÷25kGy and power dD_γ/dt=0.40Gy/s by atomic-force microscopy method in the unit СЗМУ-ЛІ5. It is determined that in comparison with the composition x=0.01, in the composition x=0.04 there occurs a decrease in the size of the crystals which can be explained by the fact that with an increase in the Mn concentration there is an insignificant decrease in the lattice parameters, which leads to a decrease in the crystal size. It is established that the irradiation partially affects the surface morphology of the films, since it is accompanied by a decrease in the size of the crystals. Within the irradiation above 25kGy dose, deterioration in the surface morphology of the films occurs.

The effect of ionizing radiation on the electrophysical, optical and photoelectric properties of $Pb_{1-x}Mn_xTe$ (x=0.01-0.06) epitaxial films has been studied. For studying the effect of the accelerated electrons on VAC, the samples were irradiated at nitrogen temperature by fast electron fluxes $\Phi \leq 7\cdot10^{17}$cm^{-2} with the energy E=4.5MeV in the linear accelerator ЭЛУ-6. A linear part $J\sim U$ corresponding to Ohm's law, quadratic $J\sim U^2$ and $I\sim U^3$–U^4 parts corresponding to a rapid increase of the current are observed in VAC of the initial samples at the temperature T=80-210K. Although the nature of the dependencies did not change, a parallel shift of the curves was observed in the direction of the current increase over the whole studied stress region at the temperature increase to T=210K. Linear section is observed in the field region E=10-10^2V/cm, and quadratic one in the field region E=10^2-10^3V/cm. As the temperature increases, the quadratic region decreases, the threshold voltage where the quadratic region begins, i.e. the voltage of the transmission from Ohm's law to quadratic, shifts to lower voltage values. A sharp increase is observed in the fields E>10^3V/cm. On the other hand, there is an increase in the current which may be due to the increase in the concentration of equilibrium charge carriers at temperature growth. A sharp increase occurs in the fields E>10^3V/cm which is mainly due to the ionization of local levels in the electric field. The nature of the dependences after irradiation by fast electron fluxes at dose $\Phi \leq 7\cdot10^{17}$cm^{-2} is shown in fig.5.

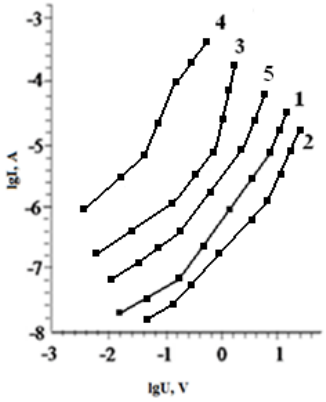


Fig.5. VAC of $Pb_{1-x}Mn_xTe$, x=0.04 thin films at T=80K: 1.Φ=0; 2.$\Phi=10^{15}$cm^{-2}; 3. $\Phi=5\cdot10^{15}$cm^{-2}; 4. $\Phi=2\cdot10^{16}$cm^{-2}; 5. $\Phi=7\cdot10^{17}$cm^{-2}

The obtained results enable to deduce that, irradiation of the crystals up to Φ=10^{15}cm^{-2}

leads to radiation defects to self-compensation and conductivity tends to its own. At $\Phi=5\cdot10^{15}cm^{-2}$ the conductivity of the samples increases as a result of decay of the neutral complexes, and at $\Phi=7\cdot10^{17}cm^{-2}$ the current, the value of which is determined by the concentration of charge carriers of the studied samples, decreases.

In order to study the effect of accelerated electrons on temperature dependence of electrical conductivity, $Pb_{1-x}Mn_xTe$ ($x=0\div0.05$) samples were irradiated at room temperature by fast electron fluxes $\Phi\leq10^{16}cm^2$ with the energy of E=4.5MeV in the linear accelerator ЭЛУ-6. It was revealed that there occurs a decrease in the conductivity after irradiation which is associated with the formation of local levels, but it should be mentioned that also, in part, with the changes in the electronic structure of the crystal, i.e. increase in the band gap width after irradiation [25, 26].

The influence of annealing on the temperature dependence of resistivity of $Pb_{1-x}Mn_xTe$ (x=0.05) $\rho(T)$ thin films after γ-irradiation (E=1.25MeV) at dose D_γ=4.9 kGy in the temperature range of 270-500K has been studied. First, the dependence $\rho(T)$ of the initial samples was measured. Further, the samples were subjected to γ-irradiation D_γ=4.9 kGy, which led to an increase in the resistivity, while the nature of the dependence and slope of the curve did not change. In order to reveal the stability of radiation defects, isochronous annealing was carried out, the duration of the first heating of the irradiated sample was 1 hour; the second annealing was carried out in 3 hours. Measurements after each annealing step were carried out at the temperature T=450K. As a result of annealing, a partial restoration of the resistivity of $Pb_{1-x}Mn_xTe$ (x=0.05) epitaxial films, irradiated by γ-quanta D_γ=4.9 kGy is observed. The obtained value of the annealing activation energy E_a, determined from the isotherms is in satisfactory agreement with the value of the activation energy for the unirradiated sample E_a=0.065eV. It can be assumed that in $Pb_{1-x}Mn_xTe$ (x=0.05) at the temperature T=450K there occurs a partial annealing of defects, creating radiation levels.

The photoconductivity (PC) of $Pb_{1-x}Mn_xT$ (x=0.02, 0.04, 0.05) thin films has been studied at the temperature T=80K. The nature of PC spectra in $Pb_{1-x}Mn_xTe$ thin films does not change, but the maxima shift towards shorter wavelengths as the amount of manganese increases: λ_{max}=5.4μm for x=0.01, λ_{max}=4.1μm for x=0.03, λ_{max}=3.44μm for x=0.05. The values of the band gap width E_g for the composition x=0.1÷0.6 were determined from these data, which had good agreement with the literary data. It is established that the photosensitivity of the sample increases with an increase in the irradiation dose up to D_γ=10kGy, further increase in the irradiation dose up to D_γ=25kGy leads to an insignificant decrease in the photosensitivity (Fig.6) [27].

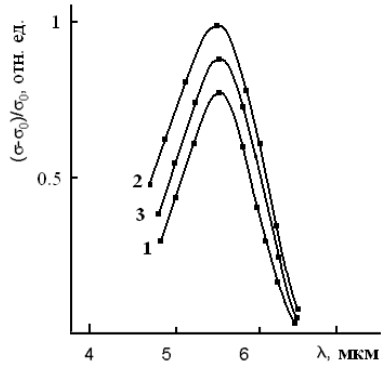


Fig.6. Spectrum of photosensitivity of $Pb_{1-x}Mn_xTe$ (x=0.02) epitaxial films at T=80K: 1. before irradiation, 2. irradiation with the dose D_γ=10 kGy, 3. irradiation with the dose D_γ=25 kGy

The effect of γ-radiation on the optical properties of $Pb_{1-x}Mn_xTe$ (x=0.01, 0.04) epitaxial films was also studied. The optical absorption spectrum of the initial crystal before irradiation is situated in the fundamental absorption region λ=2.5-6.5μm. It is shown that the edge of the intrinsic absorption moves toward the short waves with an increase in Mn concentration, which occurs due to the increase in the band gap width. A decrease occurs in the absorption coefficient within the irradiation of the samples by electron flux $\Phi \leq 10^{15} cm^{-2}$. The optical absorption edge moves to the short-wave region which leads to an increase in the band gap width from E_g=0.35eV to E_g=0.38eV. In this wavelength region, the absorbed photons have sufficient energy for excitation of electrons from the valence band to the conduction band, and thus these photons are absorbed by the material, thereby reducing the transmittance (fig.7).

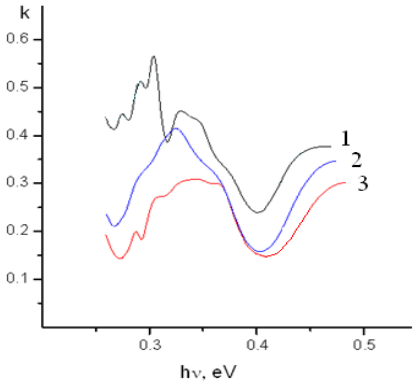
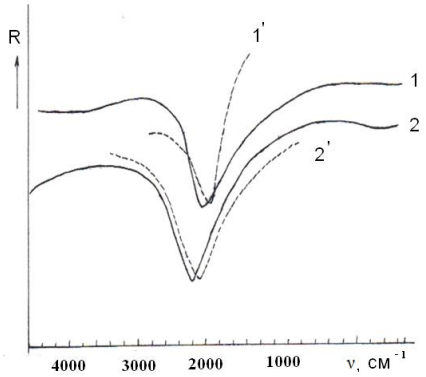


Fig.7. Optical absorption coefficient of $Pb_{0.99}Mn_{0.01}Te$ epitaxial films irradiated by electron flux: 1.Φ_1=0; 2.$\Phi_2=10^{15}$ cm^{-2}; 3.$\Phi_3=5\cdot10^{15}$ cm^{-2}.

Reflection spectra of $Pb_{1-x}Mn_xTe$ (x=0.01, x=0.04) before and after irradiation by γ-quanta at dose D_γ=205Gy were investigated with the spectrophotometer Specord -71 IR in the range of 4600÷650cm^{-1} (λ=2.2÷15 μm) at room temperature. Optical absorption occurs in the region ν=2000 cm^{-1}. It is established that Mn concentration influences the reflection spectra, since the spectrum shifts insignificantly to higher energies with an increase in Mn concentration



(fig.8).

Fig.8. Reflection spectra in $Pb_{1-x}Mn_xTe$ epitaxial films before and after γ-irradiation by the dose D_γ =205Gy: 1 (x=0.04) and 2 (x=0.01) – before irradiation, 1' and 2' – after irradiation.

Comparative study of the optical data of the initial and irradiated $Pb_{1-x}Mn_xTe$ (x=0.01÷0.04) epitaxial films shows that $Pb_{1-x}Mn_xTe$ with Mn concentration x=0.04 are the most

effective as IR detectors in the dose range of γ–irradiation D_γ=100-205Gy and electron irradiation with electron flux of $\Phi=10^{15}\div5\cdot10^{15}$cm^{-2}.

All the studies carried out on the optical properties of $Pb_{1-x}Mn_xTe$ epitaxial films are reduced to the fact that by changing both the amount of manganese and the irradiation dose in the film, it is possible to control the optical properties of the studied samples.

It has been studied the possibilities of creating isoperiodic photosensitive heterojunctions on the basis of the epitaxial films of $Pb_{1-x}Mn_xTe$, $PbTe_{1-x}Se_x$ solid solutions of various chemical compositions, corresponding contacting pairs. By adjusting the temperature of the compensating source, structurally perfect epitaxial films of *n*-$Pb_{1-x}Mn_xTe$, *p*-$PbTe_{1-x}Se_x$ have been obtained on BaF_2 single crystals by the MBC method and $Pb_{1-x}Mn_xTe/PbTe_{1-x}Se_x$ *p-n* heterojunctions, photosensitive in IR-region of the spectrum have been created on their basis in a single technological cycle, without breaking the vacuum [28].

4. Results

For the first time, ab initio calculations have been carried out for study of band structure of ideal and defective SMS $Cd(Pb)_{1-x}Mn_xTe$ (x=0.01÷0.07). It is determined that defects, such as vacancy, interstitial atom, Frenkel pair in crystal cell of $Cd(Pb)_{1-x}Mn_xTe$ lead to an increase in the band gap width, formation of additional magnetic moments, local levels in the forbidden band, and also to a change in the type of conductivity which are confirmed experimentally.

For the first time, ab initio calculations have been used for defining the defect formation energies in $Cd(Pb)_{1-x}Mn_xTe$ in different charge states depending on Fermi energy. On their basis it has been determined threshold energies and corresponding doses of stability of these semiconductors to ionizing radiation, which are confirmed experimentally.

The energy levels in GaS, GaSe, InSe semiconductors have been calculated for the anion, cation vacancies and anionic, cationic displacement by LCAO and Bond Orbital methods. It is determined that anion and cation vacancies in these semiconductors lead to the formation of local levels in the forbidden band, also local levels in the allowed band inside the valence band. It is established that the cations with a small ionic radius and tetrahedral coordination, replaced in defective semiconductors, restore the parameters of the crystal. Atoms with different coordination and large ionic radius create additional defects and local levels. Localized levels from vacancies do not disappear completely. Using this mechanism, you can not only restore the previous parameters of the crystal, but also improve its characteristics.

Epitaxial films of $Cd(Pb)_{1-x}Mn_xTe$ solid solutions with compositions of $0{,}01\leq x\leq0{,}07$ with a perfect crystal structure ($W_{½}$=90÷100") have been grown on the substrates of glass, mica and BaF_2 by MBC method in vacuum 10^{-4}Pa and optimal conditions for obtaining structurally perfect films have been determined: T_{sour}=1100-1200K, T_{sub}=570-670K, $\upsilon_к$=9÷10Å/c, T_{Te}=420÷430K

It is determined that at the temperature of substrate T_{sub}=300K the obtained $Cd_{1-x}Mn_xTe$ films on glass substrates have an amorphous structure, and on mica substrates they are polycrystalline, increase in T_{sub} (≥470 K) leads to the obtain of polycrystalline films with a cubic structure (a=6,481Å) on glass substrates, above 570 K there begins an epitaxial growth on all substrates.

It is shown that Cd(Pb)Te, $Cd(Pb)_{1-x}Mn_xTe$ epitaxial films grown with Te compensation in the growth process have a more perfect structure than without Te compensation. It is determined that after compensation of Te, the size of the particles increases, the roughness decreases and the black clusters observed on the surface disappear, which are formed during the growth process.

It has been established the optimal conditions for obtaining HJ on the basis of *n*-CdTe/*p*-

$Cd_{1-x}Mn_xTe$ (x=0.04) and n-$Pb_{1-x}Mn_xTe$/p-$PbTe_{1-x}Se_x$ epitaxial films by MBC method in a single technical cycle without breaking the vacuum by applying additional compensating source of Te vapor in the growth process. The photosensitivity of the obtained structures makes it possible to use them in the manufacture of ionizing radiation detectors, photodetectors and photoconverters based on them.

Using AFM images and histograms of the surfaces of $Pb_{1-x}Mn_xTe$ (x=0.01÷0.04) epitaxial films before and after γ-irradiation (E=1.25MeV), it has been established that irradiation of the samples up to D_γ=25kGy leads to a decrease in crystal size, within the irradiation of the samples at D_γ>25kGy there begins a deterioration of the surface morphology.

It is established that, irradiation of $Pb_{1-x}Mn_xTe$ (x=0.01÷0.05) epitaxial films by electron flux (E=4.5MeV) up to $\Phi=2\cdot10^{15}cm^{-2}$ leads to a decrease in the electrical conductivity, which is associated with the compensation of local levels. With further increase of the irradiation dose up to $\Phi=10^{16}cm^{-2}$, the electrical conductivity increases.

It is shown that, the irradiation by γ-quanta (E=1.25MeV) of $Cd_{1-x}Mn_xTe$ (x=0.01–0.07) epitaxial films at dose D_γ=300Gy leads to an increase in PC (T=300K), and irradiation of $Pb_{1-x}Mn_xTe$ epitaxial films at dose D_γ=10kGy increases the PC (T=80K), which gives ground to create ionizing radiation detectors based on them.

It has been determined that with an increase in Mn concentration in the $Pb_{1-x}Mn_xTe$ epitaxial films, and also after irradiation with accelerated electrons by the flux $\Phi\leq10^{16}cm^{-2}$, there occurs a decrease in the absorption coefficient and shift of spectrum edge towards short waves which is associated with an increase in the band gap width. This trend is also observed in $Cd_{1-x}Mn_xTe$ epitaxial films irradiated with γ-quanta up to the irradiation dose $D_\gamma\leq0.5kGy$.

5. Conclusion

The obtained results allowed solving an important scientific problem of practical importance:

- control of the structure of energy band gap of chalcogenides $Cd_{1-x}Mn_xTe$, $Pb_{1-x}Mn_xTe$ by changing the concentration of Mn, as well as GaS, GaSe, InSe through impurities;
- control of photoconductivity, magnetic momentum and type of conductivity of the crystals $Cd_{1-x}Mn_xTe$, $Pb_{1-x}Mn_xTe$ irradiating by ionizing radiation;
- obtain of epitaxial films and structures based on them with a high photosensitivity which can be used for preparing solar cells, photodetectors and ionizing radiation detectors.
- using data from the band structure and results of study of photoelectric properties of HJ, CdTe-$Cd_{1-x}Mn_xTe$ and $Pb_{1-x}Mn_xTe$/$PbTe_{1-x}Se_x$ can be used in the manufacture of low-cost solar cells, photodetectors and high-sensitivity ionizing radiation detectors.

Acknowledgment
This work was supported by the STCU Grants № 6150 and № 6288.

References

1. Romeo A., Batzner D.L., Zogg H., Tiwari A.N. Potential of CdTe thin film solar cells for space applications / 17thEuropean Photovoltaic Conference and Exhibition, 2001, Munich, Germany

2. Murphy J.W., Smith L., Galkins J., Mejia I., Cantley K.D., Chapman R.A., Quevedo -lopez M.A., Gnade B.E. Thin film cadmium telluride charged particle sensors for large area neutron detectors // Applied Physics Letters, 2014, v.105, p.112107(1-4)
3. Babalola O., Bolotnikov A., Egarievwe S., Hossain A., Burger A., James R. Effect of Te inclusions on internal electric field of CdMnTe gamma-ray detectors / SPIE Optics and photonics. San Diego, CA, 2009, August 2-6
4. Kim K.H., Bolotnikov A.E., Camarda G.S., Marchini L,, Yang G., Hossain A., Cui Y., Xu L., James R.B. Detector performance of ammonium-sulfide-passivated CdZnTe and CdMnTe materials / Brookhaven National Laboratory, 2010
5. Cui Y., Bolotnikov A., Hossaina A., Camardaa G., Mycielskib A., Yanga G., Kochanowskab D., Witkowska-Baranb M., Jamesa R.B. CdMnTe in X-ray and gamma-ray detection: potential applications / Brookhaven National Laboratory, 2008
6. Sordo S.D., Abbene L., Caroli E., Mancini A., Zappettini A., Ubertini P. Progress in the development of CdTe and CdZnTe semiconductor radiation detectors for astrophysical and medical applications / Journal Sensors, 2009, v.9, p.3491-3526
7. Smirnov L.S. Physical processes in irradiated semiconductors. Novosibirsk, Nauka, 1977, 256p.
8. Lanno M., Burguen Zh. Point defects in semiconductors. Theory, 1984, 263p.
9. Abasova A.Z., Madatov R.S., Stafeev V.I. Radiation-stimulated processes in chalcogenide structures. Baku, Elm, 2011, 349p
10. Abbasov Sh. Influence of irradiation on electrophysical, optical and photoelectrical properties of solid solutions of germanium-silicon. Baku, Elm, 2003, 207p.
11. Isayev F.K., Zaitov F.A., Matershev Y.V., Shavrov A.E.. Effect of ionizing radiation on photosensitive films of lead and cadmium chalcogenides. Baku, Elm, 1988, 71 p.
12. Mehrabova M.A., Nuriyev I.R., Orujov H.S. Electron structure and optical properties of $Cd_{1-X}Mn_XTe$ thin films // Inter. Journal of Materials, 2014, v.1, p.63-70
13. Mehrabova M.A., Orujov H.S., Hasanov N.H. Ab initio study of defects in CdMnTe: Electronic structure and related properties // Science PG Inter. Journal of Materials science and applications. 2014, v.3(6-1), p.24-32
14. Mehrabova M.A., Nuriyev H.R., Orujov H.S., Nazarov A.M., Sadigov R.M., Poladova V.N. Defect formation energy for charge states and electrophysical properties of CdMnTe // Invited paper. SPIE Photonics, Devices and Systems VI, 2015, v.9450, p.94500Q-(1-10)
15. Mehrabova M.A., Jahangirli Z.A. Band structure of defective and doped semiconductors A^3B^6 // ANAS Proceedings, 2005, №5, p.180-184
16. Jahangirli Z.A., Mehrabova M.A. Calculation of band structure of vacancies in GaSe by Green's function method // Proceedings of Higher Educational Institutions, Physics, Tomsk, 2006, №11, c.8-12
17. Mehrabova M.A. Interaction of radiation defects with impurities in layered semiconductors A^3B^6 // ANAS Reports, Baku, 2009, №4, p.78-87
18. Mehrabova M.A., Madatov R.S. Calculation of band structure of vacancies and their compensated states in semiconductors A^3B^6 // Semconductors, 2011, v.45, №8, p.1031-1037
19. Mehrabova M.A. Calculation of electronic structure of vacancies and their replacements in semiconductors $A^{III}B^{VI}$ // Radioprotection, 2008, v.43, №5, p.134
20. Mehrabova M.A. Detectors in barrier structures of metal-lamellar semiconductors // Key Engineering Materials, 2010, v.464, p.1-10
21. Nuriyev I.R., Mehrabova M.A., Nazarov A.M., Sadigov R.M., Hasanov N.H. Growth, structure and morphology of surface of CdTe epitaxial films // Semiconductors, 2017, v.51, №1, p.36-39

22. Nuriyev I.R., Mehrabova M.A., Nazarov A.M., Sadigov R.M. Surface morphology of $Cd_{1-x}Mn_xTe$ epitaxial films // ANAS Proceedings, 2015, №2, p.53-56
23. Mehrabova M.A., Nuriyev H.R., Taghiyev T.B., Sadigov R.M., Nazarov A.M., Huseynov N.I. Impact of γ-irradiation on structure and electrophysical properties of CdMnTe // Science PG, International Journal of Materials Science and Applications, 2014, v.3(6-1), p.20-23
24. Mehrabova M.A. Electrophysical and optical investigation of $Cd_{1-X}Mn_XTe$ epitaxial thin films / 8th International conference: Circuits, systems, signal and telecommunications. Tenerife, Spain, January 10-12, 2014, p.12
25. Mehrabova M.A., Nuriyev I.R. Influence of ionizing radiation on crystal structure and electrophysical properties of $Pb_{1-X}Mn_XTe(Se)$ thin films // International Journal of Energy and Environment. 2012, v. 6, p.549-556
26. Mehrabova M. A. Impact of electron-beam radiation on electrical properties of $Pb_{1-x}Mn_xTe$ epitaxial films // Science PG, Nuclear science, 2016, v.1(1), p. 1-5
27. Mehrabova M.A., Nuriyev I.R., Kerimova T.I., Poladova V.N. Impact of accelerated electron beams on photoelectrical and optical properties of $Pb_{1-X}Mn_XTe$ thin films / 5th WSEAS International conference: Nanotechnology, Cambridge, UK February 20-22, 2013, p. 305-309
28. Nuriyev I.R., Mehrabova M.A., Nazarov A.M., Sadigov R.M. Structurally perfect $Pb_{1-x}Mn_xTe$, $PbTe_{1-x}Se_x$ epitaxial films and photosensitive heterojunctions based on them // ANAS, Proceedings, 2016, №3

ВЛИЯНИЕ ИОНИЗИРУЮЩЕГО ИЗЛУЧЕНИЯ НА ФИЗИЧЕСКИЕ СВОЙСТВА ХАЛЬКОГЕНИДОВ II-IV ГРУППЫ, ЭНЕРГИЯ ДЕФЕКТООБРАЗОВАНИЯ

М.А. Мехрабова

Резюме: Проведены расчеты из первых принципов электронной структуры идеальных и дефектных полупроводников Cd(Pb)Te и Cd(Pb)1-xMnxTe методом Теории Функционала Плотности в программе Atomistix ToolKit, а также GaS, GaSe, InSe методами Связывающих Орбиталей и ЛКАО. Определены плотность состояний, ширина запрещенной зоны, полная энергия, магнитные моменты, число электронов, уровень Ферми, энергии дефектообразования и пороговые энергии.

Выявлены оптимальные условия получения совершенных эпитаксиальных пленок Cd(Pb)Te, $Cd(Pb)_{1-x}Mn_xTe$ и структур на их основе. Установлены изменения в кристаллической структуре, морфологии, в ВАХ, фотопроводимости, оптических параметрах эпитаксиальных пленок $Cd(Pb)_{1-x}Mn_xTe$ облученных γ-квантами дозой $D\gamma \leq 25$кГр и потоками быстрых электронов $\Phi \leq 7 \cdot 10^{17}$см$^{-2}$. Определены возможности создания фоточувствительных гетропереходов на основе эпитаксиальных пленок *n*-CdTe/ *p*-$Cd_{1-x}Mn_xTe$ (x=0.4) и *n*-$Pb_{1-x}Mn_xTe$/*p*-$PbTe_{1-x}Se_x$.

Ключевые слова: Расчеты из первых принципов, Теория Функционалов Плотности, метод Связывающих Орбиталей, ЛКАО, халькогениды, электронная структура, энергии дефектообразования, эпитаксия, облучение, фотопроводимость, поглощение

İONLAŞDIRICI ŞÜALANMANIN II-IV QRUP HALKOGENİDLƏRİN FİZİKİ XASSƏLƏRİNƏ TƏSİRİ, DEFEKT ƏMƏLƏGƏLMƏ ENERJİSİ

M.Ə. Mehrabova

Xülasə: Cd(Pb)Te и $Cd(Pb)_{1-x}Mn_xTe$ yarımkeçiricilərinin elektron quruluşu təməl prinsiplərdən Sıxlıq

Funksionalları Nəzəriyyəsi çərçivəsində və həmçinin GaS, GaSe, InSe yarımkeçiricilərinin electron quruluşu Rabitə Orbitalları və Atom Orbitallarının Xətti Kombinasiyası metodları ilə hesablanmışdır. Hal sıxlığı, qadağan olunmuş zonanın eni, tam enerji, maqnit momentləri, elektronların sayı, Fermi səviyyəsi, defekt əmələgəlmə enerjisi, astana enerjisi. müəyyən edilmişdir.

Mükəmməl quruluşa malik Cd(Pb)Te, $Cd(Pb)_{1-x}Mn_xTe$ epitaksial təbəqələri və onlar əsasında strukturların hazırlananması şərtləri təyin edilmişdir. $Cd_{1-x}Mn_xTe$ epitaksial təbəqələrin γ-kvantlarla $D_\gamma \leq 25$kQr dozada və $Pb_{1-x}Mn_xTe$ epitaksial təbəqələrinin $\Phi \leq 7 \cdot 10^{17}$ см$^{-2}$ elektron seli ilə şüalanması nəticəsində onların kristal quruluşunda, səth morfologiyasında, VAX, fotokeçiriciliyində və optik parametrlərində əmələ gələn dəyişikliklər müəyyən edilmişdir. Epitaksial təbəqələr əsasında fotohəssas *n*-CdTe/ *p*-$Cd_{1-x}Mn_xTe$ (x=0.4) və *n*-$Pb_{1-x}Mn_xTe$/ *p*-$PbTe_{1-x}Se_x$ heterokeçidlərinin hazırlanması imkanları öyrənilmişdir.

Açar sözlər: Təməl prinsiplər**,** Sıxlıq Funksionalları Nəzəriyyəsi, Rabitə Orbitalları metodu, Atom Orbitallarının Xətti Kombinasiyası metodu, halkogenidlər, elektron quruluşu, defekt əmələgəlmə enerjisi, epitaksiya, şüalanma, fotokeçiricilik, udulma.