Nanolamellar Structures of Oxide-$A^{III}B^{VI}$:Cd Semiconductors Type for use as Detectors of Radiation in the UV Spectral Region

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Abstract **– In the paper, optical and photoelectrical properties of *GaSe* and *InSe* single crystal films of $10^{-5}\div10^{-7}$ m submicron thickness and of semiconductor-native oxide structures obtained by annealing at (450÷700)°C in a normal atmosphere, are studied.**

The absorption spectrum of *InSe* lamella as well as of *GaSe* lamella in the energetic range from the red threshold up to 4,5 eV contains three bands with a rapid increase of the absorption coefficient which varies in the limits of ($10^0\div10^6$) cm^{-1}. At the absorption coefficients of ($10^0\div10^2$)cm^{-1} the indirect optic transitions are present.

At the energies higher than 1,25 eV and 2,01 eV for *InSe* and *GaSe* respectively the light absorption are determined by the direct optical transitions in the centre of the Brillouin zone and at the energies higher than 3,0 eV also by the direct optical transitions in the points of the bands high symmetry.

The resistive photosensitivity bands cover the spectral range $E_g \leq h\nu \leq 4{,}5$ eV for lamellar photoresistors in which electric field $E\perp C_6$. The resistive photosensitivity band width could be controlled by the lamella thickness for $d \geq 1$µm. The open circuit voltage spectral distribution is analysed from which results that at the oxidation temperature of 700°C in *GaSe* layer at the heterojunction interface the defects are formed on which the charge carriers, collected in the junction, are dissipated. The noneequilibrium charge carrier free path is of 0,8 µm.

Index Terms – GaSe, InSe, semiconductor heterojunction, oxide films, nanolamellar structures.

I. INTRODUCTION

The actual tendencies of the photonics and optoelectronic devices development are determined by the wide scale implementation of semiconductor materials. Among the perspective materials for nanoparticles fabrication and particullary of nanolamella are compounds of lamellar class semiconductors of $A^{III}B^{VI}$ type, a typical representatives of which *GaSe, GaS, InSe* and *GaTe* are [1-4].

These compounds single crystals are formed from lamellar packing of Hal-Me-Me-Hal with strong chemical binding of atoms inside of packing and weak binding (of Van-Der-Waals type) between packing [5]. The chemical binding anisotropy of the atomic plans in *GaSe* and *InSe* compounds allow by cleaving to obtain plan parallel lamella with smooth surface at atomic level, of low surface states density [6]. At a normal atmosphere the gas molecules absorption from the atmosphere occurs and at the same times an oxides layer is formed [7]. The oxides variety from *GaSe* and *InSe* compounds surface could be limited to In_2O_3 and Ga_2O_3 stable oxides by high temperature annealing of the sample [8-9]. The oxide layer from the lamella surface of p-*GaSe* and p-*InSe:Cd* is electrically positive, the fact which leads to the electron afinity decrease relative to the freshly cleaved surface by 0,35 eV in *GaSe* [5]. The high native defects concentration in lamellar crystals, determined by the atomic plans arrangement in lamellar packing and of elemntary packing to one another leads to a stability of electrical and optical properties to the ionizing radiation. These along with low surface states concentration determine one of the priority

directions of these compounds using as a photosensitive element in the radiation receivers in the visible-UV region of spectrum.

II. THE STUDIED SAPLES AND EXPERIMENT METHODICS

ε-GaSe and *γ-InSe* single crystals were grown by Bridgman method. *p-InSe* crystals were obtained by doping with 0,2 % of *Cd* during chemical compound process of synthesis. Single crystals were cuted in cylindrical blocks with the thickness of 10-12 mm and then cleaved in the lamella with the thickness of hundreds of nm up to 0,3-0,5 mm. For to simplify the cleavage procedure of the nanometric thickness lamella, the cylindrical blocks were irradiated with ultrasound during 15-20 min. The sound waves of 0,22 MHz frequency were obtained by an optical modulator made from single crystal SiO_2. The obtained *InSe:Cd* samples were oxidated in normal atmosphere at temperatures ~520°C and 580°C respectively. The heat treatment duration was chosen on the base of testing and heterojunctions with the stable in time photoelectrical parameters under the intense illumination with the radiations from the visible region of spectrum were chosen.

The electrical contacts for Hall measurements were formed by evaporation of In thin layers on (001) surface of single crystal *GaSe* and *InSe* lamella. The characteristics of *p-GaSe:Cd* and *p-InSe* single crystals determined from Hall measurements are given in the Table 1.

Spectral dependence of the photocurrent in the direction perpendicular to C_6 axis and of photovoltage in lamellar $InSe$-In_2O_3 and $GaSe$-Ga_2O_3 heterojunctions was measured

TABLE1. ELECTRICAL PROPERTIES OF CD DOPED WITH GASE, INSE

Simple	Conductivity tipe	Hall concentration (cm^{-3})	Activation energy (eV)	Mobility (cm^2 V^{-1}S^{1})
InSe:Cd	p	$8{,}5\cdot10^{14}$	0,4	28
GaSe undoped	p	p-$2\cdot10^{14}$	0,56	38÷45
GaSe-0,01%Cd	p	p-$2\cdot10^{15}$	0,24	20÷35
GaSe-0,1%Cd	p	p-$4{,}2\cdot10^{15}$	0,24	-
GaSe-0,2%Cd	p	p-$5{,}7\cdot10^{15}$	0,24	-
GaSe-0,5%Cd	p	p-$8{,}3\cdot10^{15}$	0,22	12÷20

on a unit on the base of MDR-2 monochromator. The photocurrent through the sample in the regime of photoresistor as well as through semiconductor –oxide heterojunction was calculated by potential difference on the load resistance R_s. The optical and photoelectrical characteristics of the samples in the regime of photoconductivity are connected by relation [10]:

$$G = \frac{I_{ph}}{eWlI_0(1-R)[1-\exp(-\alpha d)]} \qquad (1)$$

were the amplification coefficient, τ- is the minority charge carriers life time, tr-the electric charge "e " (electron) time of transportation through the sample, W, l- width and lenght of the sample, I0-the incident light beam intensity, R, α - reflection and absorption coefficients, d –the sample tickness.

The open circuit voltage of a heterojunction illuminated by a light bean of the intensity I_0 is given by relation [10]:

$$V = \frac{kT}{e}\ln\left(1+\frac{(1-R)I_0\left\{1-\frac{\exp(-\alpha d)}{\alpha L_n}\right\}}{\frac{D_p n_{p0}}{L_n}+N_a(v_p+S_p)\exp\left(-\frac{eV_D}{kT}\right)}\right) \qquad (2)$$

Were k-is Boltsman's constant, T-temperature, S_p-the holes recombination rate, L_0-the electron free path in p-type semiconductor, V_D-the applied to the junction voltage.

III. EXPERIMENTAL RESULTS

The elementary packing consisting of the halogen and metall atoms planar arrangement of Hal-Me-Me-Hal type in ε-*GaSe* and γ-*InSe* crystals have thicknesses of 0,8 -0,85 nm [11-12]. The presence of the weak chemical binding between chalcogenide plans allow obtaining of the lamella with the perfect surface and thicknesses needed for measurements of the absorption coefficient with a constant accuracy with the value from the units of cm^{-1} up to ~10^5 cm^{-1}. The absorption spectra of the lamella of *InSe:Cd* (curve 1) and *GaSe:Cd* (curve 2) and of lamella with a native oxide on the surface are given in Fig.1.

In the region of 1,10÷1,15 eV in *InSe* and 1,5÷2,0 eV in *GaSe* α (hν) dependencies are determined by the indirect optical transitions occur at the energies hν≥1,2 eV in *InSe:Cd* and hν>2,0 eV in *GaSe:Cd*.

The more pronounced increase of the absorption coefficient at the photons energy hν >3,2 eV which is observed (fig.1) both in initial lamella as well as after their oxidation is related to the opening of new channels of absorption in the points of high symmetry of Brillouin zone (points X, L,Σ).

Spectral dependencies of photocurrent density in *InSe:Cd* and *GaSe:Cd* lamella with low thickness are given in Fig.2. The electric field is applyed along the direction perpendicular to the symmetry axis C_6. As one can see from the comparison of Fig.1 and Fig.2 the photocurrent density in *InSe:Cd* photoresistors in the photons energy interval from the fundamental band edge up to ~4,0÷4,1 eV is increasing along with the absorption cofficient α increase. The photocurrent density is deacreasing by an order of spectral magnitude 1,2÷2,4 eV at the lamella thickness decrease from 7,3 μm to 0,8 μm. If to take into account that the absorption coefficient in this spectral region does not depend on the sample thickness (the *InSe* lamella surface perfection excludes the possibility of structural layers defected at surface formation), then one can observe that in the sample ~10% of the incident light is absorbed. The tendency of photocurrent density decrease at the photons energy *hν*>4,2 eV could be explained by the fact that in this spectral region the light is absorbed in a thin layer at the sample surface where the none-equilibrium electric charge carriers recombination rate is higher than in the sample volume. The thore rapid decrease of a photocurrent density in this spectral region indicates that the depth of the light penetration in the sample $d < L_n$ (L_n-electron free path in *p-InSe*) and more evident appears the recombination through the states on the both surfaces of the sample.

The photocurrent spectral dependencies in *p-GaSe:Cd* lamella with the thickness of 14,2 μm and 0,9 μm (Fig.3) are identical by their form for the same of p-*InSe:Cd.* The monotons photocurrent increase in the photons energy of 1,5÷1,9 eV is a results of none-equilibrium charge carrier generation at a indirect optical transitions.

The photocurrent spectral dependencies in *InSe* and *GaSe* lamella are in good correlation with the formula 1, the fact which indicates that at the electric field in the sample 10÷100 V/cm the amplification coefficient of charge carriers *G* is a constant value and at the same time the surface recombination rate of charge carriers in the single crystal *GaSe:Cd* and *InSe:Cd* lamella is rather low.

It is well known that the electrical conductivity of Ga_2O_3 films depends on oxygen atoms concentration as a dopant. At the oxidation at temperatures (450-500)°C Ga_2O_3 layers of high electrical conductivity are obtained. The majority charge carrier (electron) concentration is of (10^{17}÷10^{18})cm^{-3} and their mobility of (40÷80) cm^2/V·s [13]. At the annealing at high temperature (~900°C) the dielectric Ga_2O_3 film could be obtained.

The open circuit voltage spectral distribution normed to the number of incident photons for heterojunctions with Ga_2O_3 dielectric film and oxide film obtained at 480°C (curve 1) and 700°C (curve 2) is given in Fig.4.

As one can see the $U_{oc}=f(h\nu)$ dependencies for the analyzed structures are in good correlation with the formula

(2). The rapid increase of the open circuit voltage in the photons energy (1,85÷2,03) eV is due to the exponential

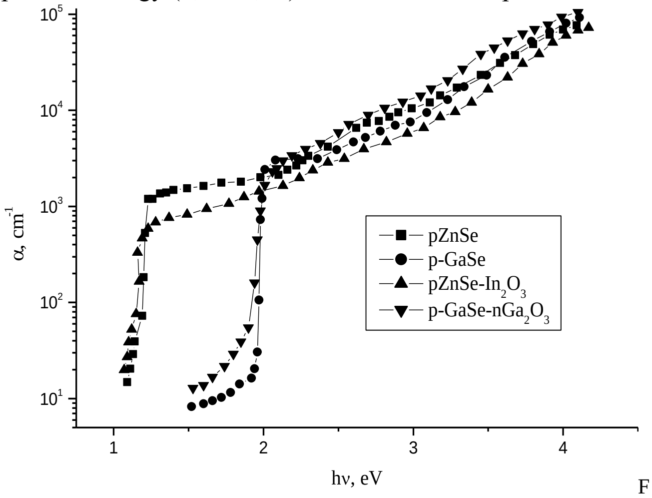

Fig.1. Absorption spectra calculated according to formula (1) from the measurements of transparency of p-InSe:Cd lamella (curve 1), In2O3-InSe (curve3), p-GaSe (curve 2), p-Ga2O3-iGa2O3-pGaSe (curve 4).

increase of the absorbtion coefficient in the region of the fundamental band edge (Fig.1, curve 2). The monotonons increase of the open circuit voltage with the photons energy increase in the region of (2,03÷4,1) eV in the heterojunction fabricated at the 480°C indicates to a low concentration of recombination centres for the minority charge carriers at Ga_2O_3-*GaSe* the result which is in a good agreement with the photoconductivity spectrum.

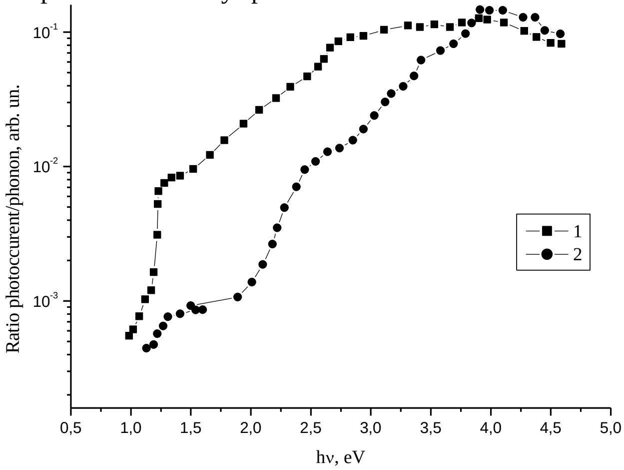

Fig.2. The photocurrent normed to the number of incident photons as a function of the photons energy for InSe:Cd lamella of the thickness of 7,3 μm (curve 1) and 0,8 μm (curve 2).

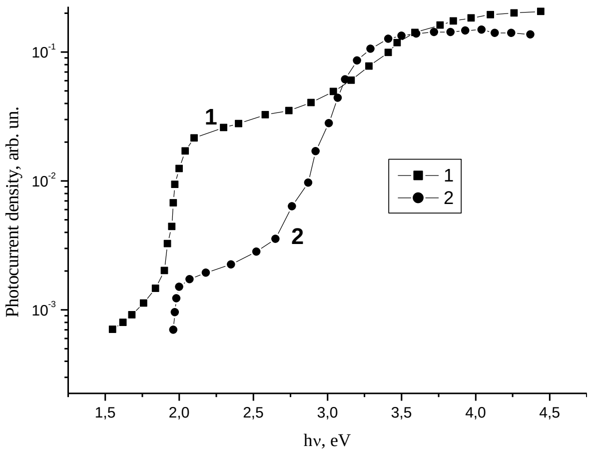

Fig.3. Photocurrent density spectral dependence in GaSe:Cd lamella with the thickiness of 14,2 μm (curve 1) and 0,9 μm (curve 2) at room temperature.

So at the oxidation temperature of 480°C the concentration of the formed defects in the presence of Ga_2O_3 oxide does not exceed their concentration on a free surface of *GaSe* lamella. The open circuit voltage rapid decrease at the photons energy *hν*>4,0 eV is due to the increase of the reflection coefficient from Ga_2O_3 layer surface (n≈3,3 [14]) and from Ga_2O_3-*GaSe* interface due to the optical transitions in the *X* point of the Brillouin zone.

The open circuit voltage spectral dependence of nGa_2O_3-iGa_2O_3-*pGaSe* structure with an oxide film made at 700°C represents a curve with the maximum at *hν*≈2,5 eV and a monotonous decrease for photons energy *hν*>2,5 eV. The minority charge carriers free path in the none deformed *GaSe* lamella, detrmined from the photocurrent relaxation analysis of the illumination of the sample back with the short pulses of the monochromatic light (by method described in [14]) is comensurable with the *GaSe* lamella thickness in the heterojunction. For the none-equilibrium charge carriers free path of this value the open circuit voltage U_{oc} should be in a direct accordance with α *(hν)* dependence. The monotonous decrease of U_{oc} in the region of photons energy *hν*>2,5 eV with the tendency of saturation at high energies indicates to the lower values of the generated carriers diffusion lenght in *GaSe* lamella.

From formula (2) one can see that $U_{oc}(h\nu)$ dependence has a tendency of decreasing with the incident radiation wavelength increase for a constant recombination rate at the interface it de curvature depth of the bands in *GaSe* $d<L_n$. For $\alpha d_n<<1$ and S_n independent on the photons energy from (2) one can see that the open circuit voltage monotonously decreases along with the [15] factor.

$$\alpha I_0 / (\alpha L_n + 1) \quad (3)$$

By varrying the monochromatic radiation intensity ΔI_0 so that to maintain constant the open circuit voltage value, the minority charge carriers free path could be determined.

The results of measurements of intensity variation ΔI_0 of the incident beam as a function of inversly of the absorption coefficient at energies from range (3,0÷ 4,0) eV are presented in Fig.5. The relatively low free path L_n value of 0,8 μm indicates that at 700°C at Ga_2O_3-*GaSe* interface a native structural defects and new phases (Ga_2Se_3, *GaO*) are formed which serve as dissipation and recombination centres of non-equilibrium charge carriers on *GaSe* lamella surface.

The band diagram of nGa_2O_3-iGa_2O_3-*pGaSe:Cd* heterojunction calculated on the base of absorption and photoconductivity spectra and measurements of charge carriers concentration in *GaSe* and Ga_2O_3 lamella is brought in Fig.6. The band curvature value in the *pGaSe*-iGa_2O_3 contact region was determined in [14] from the measurements of C-V characteristics.

IV. CONCLUSION

By decreasing the GaSe and InSe single crystal lamella thickness one can control the transmission band of them.

The absorption fundamental band edge of InSe and GaSe single crystal lamella is determined by the indirect optical transitions with the absorption coefficient α <100 cm^{-1}.

By varrying the GaSe and InSe lamella thickness in the submicron range one can fabricate the radiation detectors with a sensitivity in the UV-region of the spectrum.

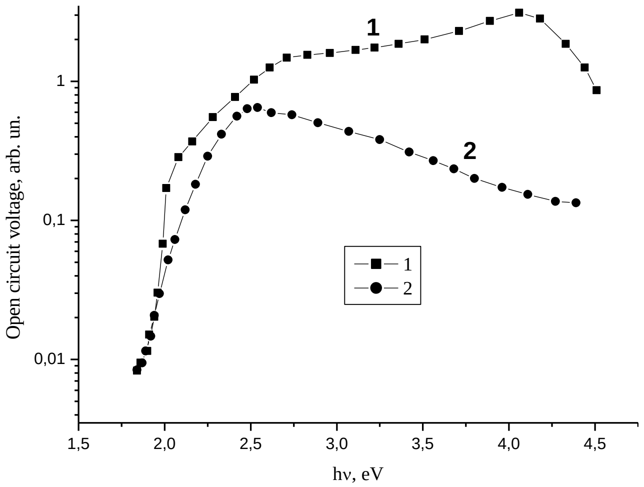

Fig.4. Open circuit voltage spectral distribution of pGa_2O_3 iGa_2O_3 – nGaSe heterojonctions with a layer of native oxide obtained at 480 ºC (curve 1) during 90 min and at 700 ºC (curve 2) during 90 min in a normal atmosphere. The GaSe lamella thickness is of 11,5 μm

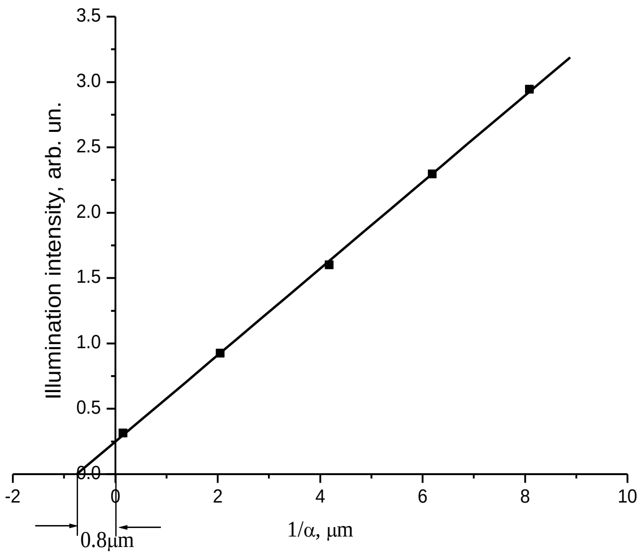

Fig.5. Determination of diffusion free path in nGa_2O_3 iGa_2O_3 – pGaSe with a native oxide layer made at 700ºC during 90 min in a normal atmosphere.

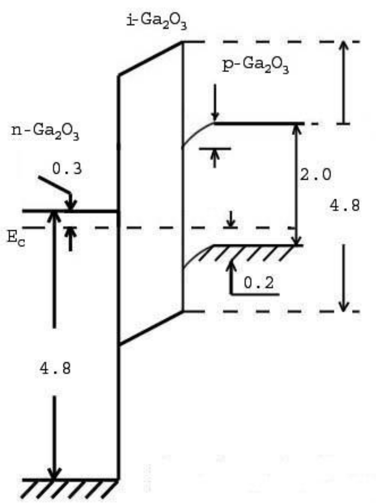

Fig.6. Band diagram of *nGa_2O_3-iGa_2O_3-pGaSe:Cd* heterojunction

The recombination centres and surface states density in the oxide-GaSe region depends on the surface oxidation temperature. The surface defects concentration does not change at the heat treatment at 480°C. At the GaSe surface oxidation temperature of 700°C in the oxide-GaSe contact region structural defects which diminishes the minority charge carrier free path up to 0,8 μm are created.

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