THE DETECTORS OF UV AND X RADIATION BASED ON Ga_2S_3 AND GaSe SEMICONDUCTORS INTERCALATED WITH Cd

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There are presented absorption of light, photosensitivity and roentgen spectra at the temperature of 78 K and 293 K of Ga_2S_3 and GaSe crystals as well as crystals intercalated with Cd. The direct band gap of Ga_2S_3 crystals intercalated with Cd is equal to 3.15 eV (78K) and respectively 3.407 eV at the temperature of 78 K. The indirect bandgap of Ga_2S_3:Cd is 2.99 eV (293 K) and at the temperature of 78 K is 3.05 eV. The maximum photosensitivity band of the compounds based on Ga_2S_3 crystal is 3.45 eV and forGa_2S_3:Cd photoresistor is 3.60 eV. The photosensitivity band of the UV detectors is in good agreement with the edge of the absorption band of ozone in the atmosphere. Resistors based on Ga_2S_3:Cd and GaSe have high sensitivity to X-rays. The roentgen current linearly increase at the exposure to K_α radiation (1.5406 Å).

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1. Introduction

One of the most important problems of semiconductor materials used in photoelectronics is the development of compounds with stable properties at the influence of UV, X-ray and γ radiation as well as the development of detectors for ionizing radiation based on these materials. The structural defects in the material are induced under the action of UV, X-ray and γ radiation. The concentration and the type of these defects depend on both, the dose of radiation and of the nature of the material [1]. The detectors of X-ray and UV radiation based on these materials have to comply the condition that the concentration of their own defects is much higher than the concentration of the defects induced by radiation [2]. Materials such as $A_2^{III}B_3^{VI}$, particularly Ga_2S_3, meet this requirement. The 1/3 of nodes is vacancies in the crystal lattice of these materials [3]. The concentration of own defects in these materials is about 10^{22} cm^{-3}. The $Ga_2S_3$is a compound with a wide band gap (E_g=3.3 eV) [4]. The electrical conductivity of Ga_2S_3single crystals at normal temperature is about $10^{-12}\Omega^{-1}cm^{-1}$. Among the factors that determine the threshold of photoreceptors sensitivity is the internal series resistance of detector [5].

The GaSe with high sensitivity in the visible and UV region of spectrum is a prospective semiconductor for the photoelectronics. Monocrystals of this material are composed of planar packages of Se-Ga-Ga-Se with covalent bonds inside the packing and weak links between packages due to polarization forces [6]. The concentration of their own structural defects is much higher than the concentration of free charge carriers in the material due to a few particular properties [7]. The specificity of these chemical bonds inside the packing and between packages allows us to obtain surfaces with the density of surface states of $10^{10}cm^{-2}$ by the splitting of massive crystals [8].

The electrical conductivity of the $Ga_2S_3$and GaSe has to be increased without any other changes of the materials' basic physical characteristics (bandgap, the diagram of recombination

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levels, lifetime of non-equilibrium charge carriers) for efficient photodetectors of UV and X radiation.

The paper presents the research results of the photoresistance properties of Ga_2S_3 and GaSe:Cd compounds.

2. Experimental

The Ga_2S_3 and GaSe compounds were obtained from the elementary component of Ga(5N), Se (5N) and Sulfur in stoichiometric amount. The synthesis temperature of Ga_2S_3 was 1250 °C and 1100 °C for GaSe. The p-type GaSemonocrystals were grown by Bridgman method. The concentration of the holes at a temperature of 330 °C was $3.5 \oplus 10^{13}$ cm^{-3}.

The Ga_2S_3 mono-crystals for photoelectric detectors were obtained using the method of molecular transport where iodine (I_2)being used as a carrier. The primary material used for transport was synthesized Ga_2S_3 (5g). The electrical conductivity of the obtained Ga_2S_3 mono-crystals was $(5\text{-}7)\cdot 10^{-12}\Omega^{-1}cm^{-1}$. The electrical conductivity of β-Ga_2S_3monocrystalsincreases to 3 orderswhen the Cd from the vapor phase is intercalated. Samples for photoelectric measurements were cut from GaSemonocrystal plates intercalated with Cd in the vapor phase. As a result of intercalation, the electrical conductivity of surface ofGaSe plates increased by ~ 1.5 times from $1.8 \oplus 10^{-8}\Omega^{-1}cm^{-1}$ to $3.1 \oplus 10^{-8}\Omega^{-1}cm^{-1}$. The X-rays detectors were developed from GaSemonocrystal plates with the thickness of 6.1 mm and Ga_2S_3 which thickness was 2.8 mm. The GaSe and Ga_2S_3 plates were cut from massive crystals. Then the rectangular prisms surface with the area of (5×4) mm^2 for GaSe and (2.5×3.6) mm^2 for Ga_2S_3 were cut. Samples were treated for 60 minutes in a steam of Cd ($2mg/cm^2$) at the temperature of 480 °C. The thin layer of indium (In) obtained by evaporation in vacuum method was used as the electrode on the surface of β-Ga_2S_3 and GaSe lamellas. The In electrode was used forpure β-Ga_2S_3, intercalated with Cd and GaSe lamellas. The specific resistivity of GaSe:Cd samples was $2.3\cdot 10^6\Omega\cdot cm$ and for Ga_2S_3(Cd) samples was $7.5\cdot 10^8\Omega\cdot cm$. The current through the sample at a voltage of 24 V was recorded by the electrometer (V7-30) with the input resistance of 10^{14} Ω.

There were measured the current-voltage characteristics for pure Ga_2S_3, Ga_2S_3 intercalated with Cd with the size of (2x5x3) mm^3 and GaSe which size was (4x8x3) mm^3. In Table 1 there are presented the temperature condition of intercalation, the electrical conductivity of the intercalation and the specific resistivity at the dark and lighting with 200 Lx from a white light source.

Table 1 - The intercalation parameters.

Material	Intercalation temperature, °C	Treatment duration, hours	The Cd concentration, mg/cm^3	Electrical conductivity, $\Omega^{-1}cm^{-1}$	Ratio R_l/Re (E=200Lx)	Type n/p
Ga_2S_3	-		2	$5{,}8\cdot 10^{-12}$	28	n
	350	12	-	$9{,}1\cdot 10^{-12}$	24	-
	450	12	-	$6{,}3\cdot 10^{-12}$	8,0	-
	550	12	-	$2{,}6\cdot 10^{-12}$	10,2	-

The absorption coefficient for Ga_2S_3 mono-crystals wascalculated from transmittance (t) and reflectance (R) measurements at the angle of α≤10°. The absorption coefficient α was determined from the equation[9]:

$$t = \frac{(1-R)^2 exp(-\alpha d)}{R^2 exp(2\alpha d)} \quad (1)$$

where d is the sample thicknesson the direction of light propagation.

The t, R coefficients and photocurrent through the sample (I_x) function of wavelength were measured using the device based on monochromator with a high-resolution power (1meV). Photosensitivity was determined as the ratio of the photocurrent to the number of incident photons on the sample. The energy of incident monochromatic beam of radiation on the sample was measured with a Vth-1 thermocouple with KBr window.

3. Results

The edge of the absorption band of the Ga_2S_3crystals that were treated at the temperature of 480 °C in Cdvapors for 12 hours is in the range of 3.0 to 3.2 eV. The spectral characteristics $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ are presented in Fig. 1. The band gap was determined by extrapolation to $\alpha = 0$, whereα - absorption coefficient was in cm^{-1}.

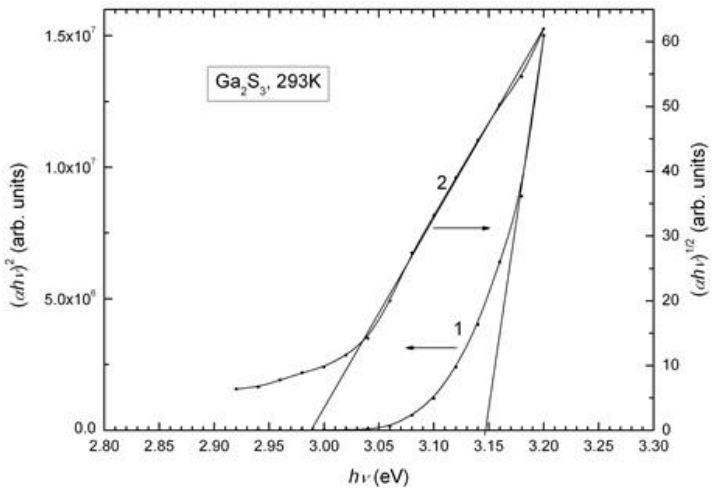

Fig. 1.The spectral characteristics $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$at the temperature of 293 K (curve 1 – Ga_2S_3, curve 2 – Ga_2S_3 intercalated with Cd).

The indirect band gap is equal to E_{gi}=2.99 eV and direct band gap is 3.15 eV. The shift of the edge of the absorption band to ultraviolet (UV) range of spectrumtakes place when the temperature of the sample decreases from 293 K to 78 K (Fig. 1 and Fig. 2).

The Ga_2S_3 compound intercalated with Cd (Fig. 2) represents the material in which take place direct and indirect optical transitions. At the temperature of 78 K the Ga_2S_3 crystals intercalated with Cd have the indirect band of 3.05 eVand direct band of 3.407 eV. Note that the optical bandwidth of α-Ga_2S_3 crystals at room temperature is equal to 3.4 eV[4]. The presence of iodine introduced in the growth of Ga_2S_3mono-crystals as well as intercalated Cd leads to displacement of optical band with 0.25 eVto lower energies.

In Fig.3 are shown the spectral dependencies of the photocurrent at the temperature of 300K for Ga_2S_3 (curve 1) and Ga_2S_3 intercalated with Cd (curve 2). The thickness of $Ga_2S_3$is 470 μmwith surface area of 4.3 mm^2 and the thickness of Ga_2S_3:Cd is 350 μmwith surface area of 4.8 mm^2.

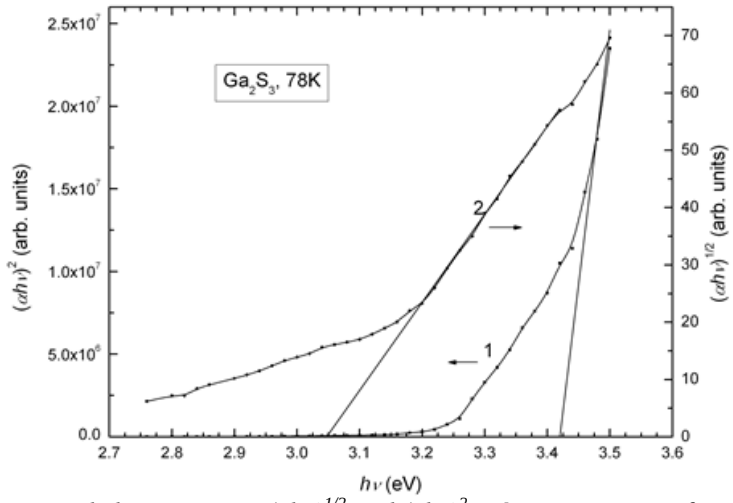

Fig. 2.The spectral characteristics $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$at the temperature of 78 K (curve 1 - Ga_2S_3, curve 2 – Ga_2S_3 intercalated with Cd).

The photosensitivity band at the half ofphotocurrent maximum intensity is 0.5 eVfor pure crystals and 0.8 eV for samples intercalated with Cd. It is also noted that the intercalation of Ga_2S_3 crystals with Cd shifts the photosensitivity peak to high-energiesfrom 3.60 eV to 3.45 eV. The maximum of photocurrent increase for approximately 30 times. The relaxation time of the photocurrent in UV-detectors based on β-Ga_2S_3ismuch higher (14s) than for Ga_2S_3detectors intercalated with Cd($1.55\cdot10^{-3}$s). Also, the own noise of voltage at the temperature of 300 K is 3.6 V for $Ga_2S_3$and 1.4μV for Ga_2S_3mono-crystal intercalated with Cd.

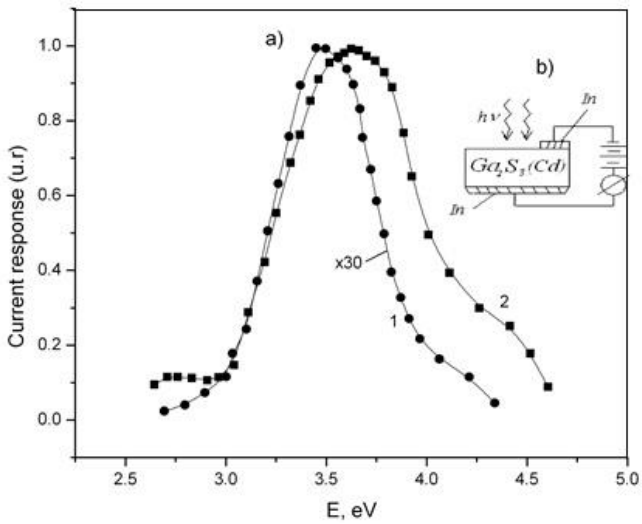

Fig. 3.The spectral dependencies of the photocurrent at 300 K for Ga_2S_3 (curve 1) and Ga_2S_3 intercalated with Cd atoms (curve 2).

Therefore, the photoresistor with longitudinal photoelectric effect (the photocurrent and light are collinear) based on Ga_2S_3mono-crystals intercalated with Cdin vapor phase may be used as a detectors of radiation at the edge of electronic absorption band of ozone in the atmosphere.

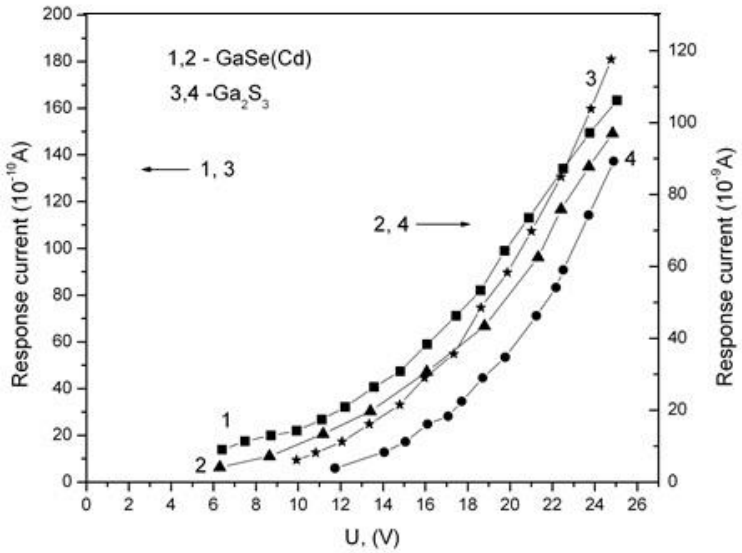

Fig.4.Current-voltage characteristic for different X-ray fluxes for GaSeand Ga_2S_3 receivers: 1,2-GaSe:Cd; 3,4 - Ga_2S_3; 1,3- Iac=8mA; Uac=45kV; 2,4 - Iac=5mA; Uac=45kV.

In Fig. 4 there are presented the current-voltage characteristics of samples at the irradiation with $Cu_{K\alpha}$ radiation (λ = 1.5406 Å) at a constant acceleration voltage of 45 kV and the intensity of current in the X-ray tube of 5 mA and 8 mA.

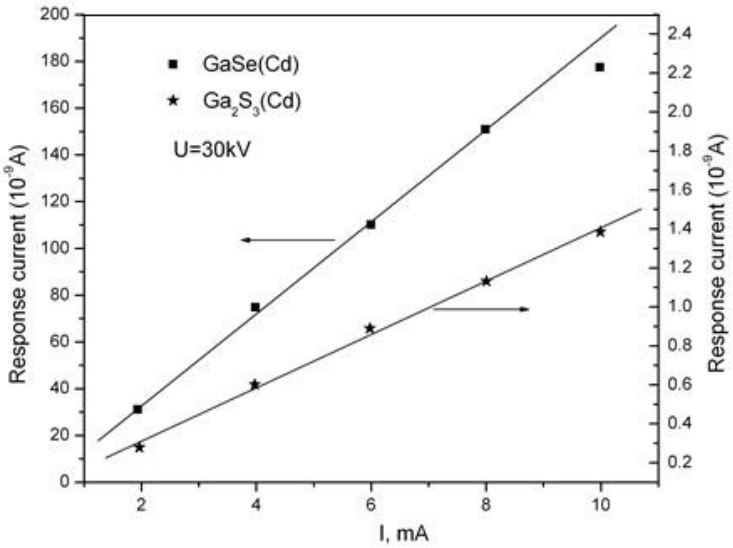

Fig. 5.Response current for different exposure

In Fig. 5 there is shown the characteristics of current generated by β-$Ga_2S_3$and Ga_2S_3 intercalated withCd detectors on the currentin the tube with Cu anti-cathode forconstant accelerating voltage of 30kV. As shown in Fig.5, the response of the detector linearly depends on the current in the X- ray tube (I_x).

Since theintensity of X-ray beam is proportional to the current in tube (I_x), it can be concluded that the response of X-raydetectors in GaSe and Ga_2S_3 intercalated withCdlinearly depends on irradiation of $Cu_{K\alpha}$ (λ = 1.5406 Å). The slope of the current-exhibition [I_x(IR)] characteristic (the parameter that determines the receiver sensitivity) depends on the material from which is made the detector. It is equal to $1.8\cdot10^{-10}$rel. units for GaSe and $1.4\cdot10^{-10}$rel. units for Ga_2S_3resistor.

The linear dependence of the signal detected by the radiation dose and current generated by the detector are two factors that determine the applicability of X-ray detectors in various areas such as environment, medicine, biochemistry and others.

4. Conclusions

The transverse structures based on semiconductorswith their own structural defects and wide bandgap (Ga_2S_3) can be used as detectors of the UV radiation.

The maximum of photosensitivity band of Ga_2S_3 is 3.45 eV and shifts to high energies by 150 meV for Ga_2S_3detectors intercalated with Cd.

The crystal plates ofGaSeand Ga_2S_3 intercalatedwith Cd with thickness from 3 mm to 5 mm are linearly sensitive to the X-ray dose withthe wavelength of $\lambda = 1.5406$ Å.

The sensitivity of detectors based on GaSe compounds is 1.3 times higher than the sensitivity of Ga_2S_3receiver.

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