$A^{III}B^{VI}$ PHOTOVOLTAIC RECEPTORS FOR EXPERIMENTAL DETERMINATION OF CARBON COMPOUNDS IN ATMOSPHERE

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Abstract: This paper examines the prospects of using semiconductor layered $A^{III}B^{VI}$ type - photovoltaic cells and the photoresistors as receptors for quantitative and qualitative measurements of carbon oxides. Carbon compounds in gaseous state form absorption bands of electromagnetic radiation in a wide range of spectrum (200 ÷ 100 000) cm^{-1}. The light absorbed or emitted in these bands at the excitations with ionizing radiation (X, γ) or strong electric fields contain direct information about the concentration of these molecules. The frequencies that correspond to maxima of these bands are characteristic parameters of absorbing molecules. Fundamental absorption bands of CO, CO_2 and NC have the edge of band at the border of ultraviolet-vacuum, while the emission bands *d* cover their full range of wave numbers from 45000 cm^{-1} to 10000 cm^{-1}. Two types of radiation receptors from lamellar semiconductor type $A^{III}B^{VI}$ photosensitive in this spectral range are studied.

Keywords: photovoltaic receptors, carbon, atmosphere, absorption band, energy, light, receptor sensitivity

1. INTRODUCTION

Carbon is tetra-covalently in chemical combination, which allows C to combine simultaneously with electro-positive and electro-negative elements. Most commonly, carbon binds with hydrogen forming hydrocarbons with oxygen. More rarely carbon bounds to nitrogen and elements of group VII through special conditions. Carbon forms five oxides (CO, CO_2, C_3O_2, C_5O_2 and $C_{12}O_9$). Most common in the atmosphere are CO_2 and CO gases. These gases are obtained as a result of multiple chemical reactions, among them are burning of organic compounds and fermentation processes. The presence of four valence electrons stimulates the formation of a large number of halide. As a result of burning fuels with participation of sulfur impurities at high temperatures are forming carbon disulfide CS_2 and cyanide. Some compounds of nitrogen (cyanide) are forming in atmosphere at burning. Many carbon compounds are highly toxic materials (CO, CN, HCN). Automation of technological processes, particularly in the food industry, as well as the toxicity of carbon compounds causes a range of issues related to effective and efficient detection of these gases.

The paper analysis the photovoltaic properties of oxide-semiconductor thin films $A^{III}B^{VI}$ with CO and CN. These thin films are used for photovoltaic cells and as receptors for quantitative and qualitative measurements of carbon oxides [1]. Two types of radiation receptors from lamellar semiconductor $A^{III}B^{VI}$ were studied [2].

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The optical absorption or emission spectroscopy methods based on electronic spectra have revealed among analytical methods of study of gas mixtures. The electronic absorption bands of carbon oxides (CO, CO_2), cyanide and carbon sulfides are situated in deep UV and UV border –vacuum range of spectrum. The emission bands (fluorescence, photoluminescence) cover the whole range of UV-visible-near IR. To CO_2 molecule corresponds a discrete bands system situated in the range of (6000 - 3000) Å. The bands can be well identified in the carbon oxide flame. These bands are interpreted as the transition between excited electronic levels. A system of emission bands at electric discharge in gas is in the range of (2900 - 5000) Å. This system of bands is characteristic for ionic molecules of CO_2^+**.** Emission bands of CN and CO molecules also are situated in this spectral range [3-4]. The sensitivity of probing and recording method for oxides, nitrites and other gaseous compounds of carbon depend on the physical characteristics of the receiver.

2. EXPERIMENTAL

Stratified semiconductor of GaSe and InSe with band gap of E_g = 2.0 eV and respectively Eg = 1.2 eV was used for photovoltaic photoreceptors sensitive in the wavelength range of 200 nm to 1000 nm. The second element of heterojunction was own oxide of ($Ga_2 O_3$), In_2O_3 as well as zinc oxide (ZnO) and Sn (SnO_2).

The monocrystals of GaSe and InSe:Cd were grown by Bridgman method [5]. The holes concentration of these crystals (p type) was $3x10^{14}$ cm^{-3} at 300 K. The p-GaSe was obtained by doping with 0.1% at Cu in stoichiometric quantities. The optical homogeneous plates were prepared with thickness of 20 μm to 30 μm. The oxidation of GaSe and InSe plates occurred in normal atmosphere at temperature of 300° C - 600 ° C and T =450° C -700° C depending of treatment duration (0.5 - 1) h. The ZnO optically transparent layer on GaSe surface (0001) was obtained by thermal oxidation of semitransparent Zn film in vacuum at pressure of $5x10^{-5}$ Torr. The In and Ni were used as electrodes on InSe surface and respectively GaSe surface.

The sensitivity of bands for receiver (heterojunction-oxide- GaSe or InSe semiconductor) was adjusted with absorption or emission bands of analyzed gas using assembled interferential filters directly on surface of optically transparent electrode. The interference filters were composed of two Al mirrors which transmission coefficient at λ = 500 nm was 35%. The MgF_2 layer separated the mirrors. The thickness “t” of MgF_2 was determined from relation:

$$t = \frac{k\lambda_{\max}}{2n} \tag{1}$$

where n - refractive index, k - the order of interference.

3. RESULTS AND DISCUSSION

The Ga_2O_3-GaSe:Cu-Ni, In_2O_3-InSe:Cd-In and ZnO-GaSe-Cu-Ni heterojunctions were obtained on GaSe monocrystalline plates doped with 0.1 % at Cu and on InSe doped with 0.2 % at Cd. The concentration of vacancies in the compounds based on GaSe was p = $3.2x10^{16}$ cm^{-3} and mobility of 40 cm^2/Vs. The Cd forms in InSe a few acceptors that at small concentrations compensate their own donors. For concentrations bigger than C≥0.1 % at transforms the electrical conductivity of semiconductor in to electrical conductivity through holes.

The presence of Ga_2O_3 oxide layer on (0001) surface of GaSe and In_2O_3 plates was identified by diffractometry of Cu K_α radiation (λ=1.540 Å). The intense peaks 2Θ equal to 14.90 ° (002), 15.714 ° (100) and 35.17° (111) are characteristic to diffraction from atomic planes of Ga_2O_3 oxide. Similarly, were identified the presence of ZnO layer at the oxidation of Zn film on (0001) surface of GaSe monocrystalline plate.

The photoresistor samples were obtained by cutting rectangles with surface area of (3x7) mm^2 from GaSe monocrystalline plates undoped and doped with 0.05 % at of copper. Identical samples were prepared from InSe plates undoped and doped with 0.2 % at Cd. The thin films of In deposited by vacuum doping were used as electrodes for photoresistors.

The spectral characteristic of photosensitivity (photocurrent density relative to absorbed photon) for GaSe and GaSe:Cu with 0.05 % at Cu photoresistors are presented in Figure 1. As shown in this figure, a range with high photosensitivity occupies spectral range from 2.0 eV (620 nm) to 3.7 eV (335 nm). We note that in the range with maximum photosensitivity (~ 360 nm) the photocurrent density normalized to a photon in GaSe photoresistors doped with Cu was 15 times higher than for photoresistors based in pure GaSe.

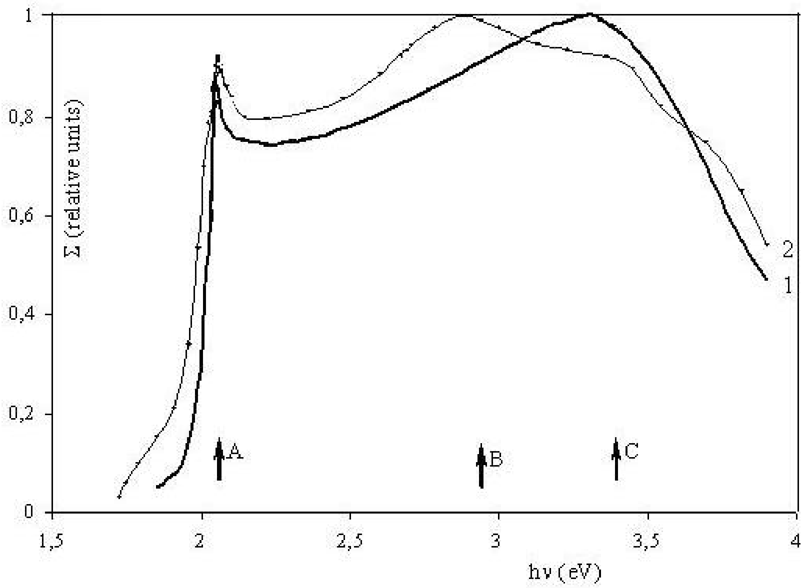

Fig. 1. The spectral distribution of photosensibility of photo-resistors: GaSe (curve 1) and GaSe:Cu (C=0.05% at Cu) (curve 2).

The photosensitivity spectral characteristics in short circuit mode for solar cells based on ITO-Ga_2O_3-GaSe:Sn, ITO-GaSe-Cu and ZnO-p-GaSe heterojunctions are shown in Figure 2.

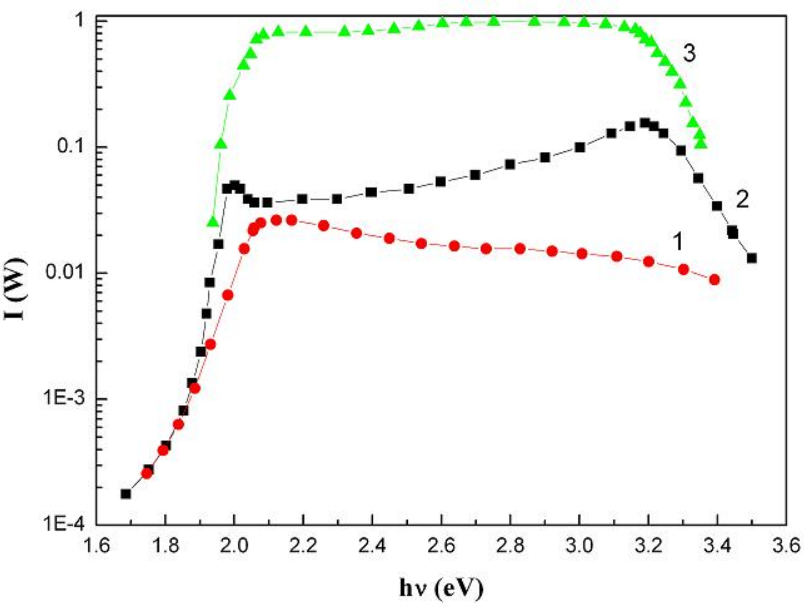

Fig. 2. The spectra of photocurrent ratio to photons energy at the temperature of 293 K for heterojunctions: ZnO-p-GaSe(curve 1); ITO-GaSe:Cu (curve 2); ITO-Ga_2O_3-GaSe:Sn (curve 3).

As shown in Figure 2, by replacing the layer of In_2O_3 with ZnO layer broadens the spectral range in red region up to 1.7 eV (730 nm) [6]. Radiation receiver with constant sensitivity within wavelengths from 620 nm to 364 nm is obtained. Violet edge of the photosensitivity is determined by the absorption band of zinc oxide. Sudden decrease of photosensitivity for ITO-Ga_2O_3-GaSe:Sn photoreceptors at photon energies higher than 3.2 eV (λ <400 nm) is determined by the increase of absorption coefficient of Ga_2O_3 layer of the heterojunction.

Spectral region of photosensitivity for receptor can be extended up to ~ 1.1 eV (1100 nm) by replacing the GaSe semiconductor with InSe.

In Figure 3 (curve 1) is presented spectral characteristics of photocurrent normalized to a photon function of energy. The photoresistor based on InSe has constant photosensitivity from 1.2 eV (1000 nm) to 2.0 eV (620 nm). From fig.1 and fig.3 results that photoresistors based on InSe and GaSe:Cu provides a non-selective photosensitivity in a fairly wide range of energies from 1.2 eV (1000 nm) to 3.4 eV (360 nm). The necessity of additional source of direct current and a high threshold for current fluctuations are the technical factors that limit the application of photoresistors as receivers in the near infrared region up to the ultraviolet region of the spectrum. A high threshold for current fluctuations is driven by high electrical resistance (10 - 100) kΩ of resistor. This drawback is avoided in photovoltaic cells based on p-InSe.

In Figure 3 (curve 2) is presented relative photosensitivity spectral characteristics of solar cell In_2O_3-InSe:Cd (0.05 % at). Spectral range of photosensitivity of these receivers is limited by InSe photons absorption band at low energies and at high energies by absorption coefficient at photon energy bigger than $h\nu \geq 3.2$ eV. Photosensitivity limit for receptors, both photoresistive and photovoltaic (with heterojunction) is determined by two parameters: spectral bandwidth and noise level. Random noise can be decreased by decreasing the internal resistivity of photosensitive unit. Recorded spectral bandwidth of the receiver was adjusted by the emission bandwidth of the analyzed molecules with an interferential filter with a thin layer of MgF_2 dielectric. The thickness of dielectric layer was 0.15 μm for interferential filter with maximum optical transmittance at the wavelength corresponding to vibrational band v'=2→v"=0 ((λ = 124 Å) of electronic emission spectrum of carbon monoxide (CO) molecule.

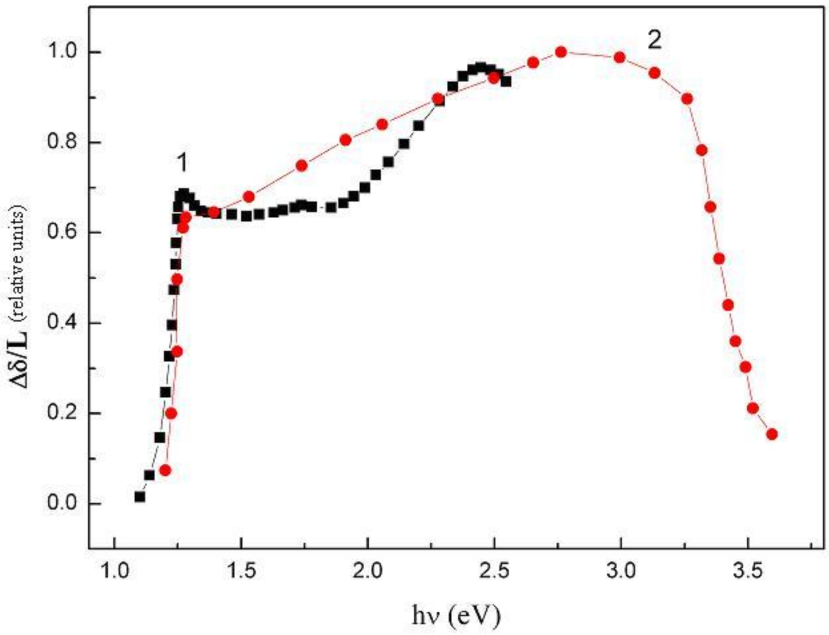

Fig. 3. The spectral dependence of photoconductivity of InSe photoresistor (curve 1) and photosensibility of In_2O_3-InSe:Cd (curve 2).

Intensity of light beam at the wavelength of λ = 4124 Å of maximum emission band (v'=2→v"=0) for CO molecules was determined by measuring the intensity of incident light (I_0) and transmission thorough filter (I_t) and it was 32%. The maximum intensity transmission path is ~ 1 for the ideal mirrors interferometer with transmission coefficient equal to 0.35 and total reflection for mirror of 0.7. The difference between these two values is due to heterogeneity of MgF_2 layer thickness of interferometer and the presence of significant absorption of filter mirrors. The transmission band of filter with order k = 2 is at λ ~ 820 nm and as shown in Figure 2 the photovoltaic cell based on GaSe did not record it. The ensemble of interferential filter based on

GaSe or InSe and photoreceptor can be adjusted by varying the thickness of MgF_2 dielectric layer to record the emission bands from electronic spectrum of CO gases.

4. CONCLUSIONS

Spectral characteristics of photosensitivity were studied for photoresistors based on GaSe and InSe layers doped with Cu (0.1% at) and respectively Cd (0.05% at). The photoresistors from GaSe and InSe provides measurement of emission spectra and luminescence of gases like CN, CO, CO_2 and CHN in the range of (3.5 – 1.2) eV.

The density of states at the surface of GaSe and InSe photoresistors decreases in the region of heterojunction contact oxide-metal-semiconductor (p-GaSe, n-InSe) by technological processes. The spectral sensitivity of the receptors is independent of wavelength of incident radiation in spectral range of (360 - 1100) nm.

The assembly consists of interferential filter and photoreceptor based on InSe or GaSe is adjusted to the emission band of the gas molecules like CN, CO, CO_2, CHN by varying MgF_2 film thickness of interferometer.

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