OTHER CONTRIBUTIONS

ADVANTAGES OF APPLICATIONS UV DETECTORS BASED ON STRATIFIED CRYSTALS IN MEDICINE

Academician, Professor, Dr. Hab. Ion ABABII
University of Medicine and Pharmacy "Nicolae Testemitanu"
Professor Efim ARAMA, University of Medicine and Pharmacy "Nicolae Testemitanu"

The results of elaboration, construction and implementation of ultraviolet radiation detector (UV) with high sensibility are presented, which is used as portative device for measuring of intensity and dose. Photo-receivers possess high stability at the irradiation and in connection with it have multiple practical applications, inclusively for the construction of Roentgen ray detector and of transducer for the registering of electrons fluxes density. The optimal parameters give the possibility to use the detectors in medicine, biology, ecology and agriculture.

Key words: *ultraviolet radiation detector, characteristics and parameters, mono-crystals, photosensitivity, photo-resistors, radiation receptors, photo-receiver**,** semiconductor material*

Introduction

The ultraviolet UV radiation acts effectively upon the vital activity of living organisms and plants. This fact leads to their wide application in biology, medicine, agriculture. According to the opinion [1] the radiation UV is divided in three regions: UV A, UV B and UV C. Ultraviolet A (λ=320 ÷ 400 nm) belongs to the solar light which reaches the Earth surface produces a weak erythematic effect; UV B (λ=280 ÷ 320 nm) has the action on the skin, causing a more pronounced erythematic effect followed by pigmentation; UV C (λ=220 ÷ 280 nm) has more dangerous action on the living matter.

A great majority of biological vegetable and animal media absorb the UV radiation with the wavelength shorter than 230 nm. The proteins absorb radiations with the wavelength of λ=275 nm; nucleic acids and fatties are also absorbing of UV. It is sufficient to mention, that the human eye is exposed during its life to the radiation of UV that belongs to the solar radiation spectrum. The main function of ocular anterior pole (cornea and crystalline) is that of focusing this radiation on the retina, being in the same time as an efficient filter for the UV A and UV B and protecting the retina of their dangerous action. The radiation of the wavelength λ=295 nm is absorbed completely by cornea. The crystalline absorbs radiations UV A and UV B (295 ÷ 400 nm) which crosses the cornea and can have photo traumatic effects on the structural crystalline proteins. The prolonged exposition (big dose of UV radiation on the crystalline) leads to the cumulative photochemical deterioration and leads to the actinic ophtalmia, cataract, destroys the retina and leading to the blinding. The mechanism, by which the UV A and UV B radiation produces cataract, is not so clear; the processes of biochemical nature and biological one can take place in the photochemical moment and the formation of cataract [2]. There are numerous epidemiological and laboratory studies, which demonstrate that the photons of UV radiation that touches the eye (especially UV B) are strong cataract dangerous for the human crystalline. This fact generated a great interest for the mechanism of the action of UV B radiation on the crystalline proteins, and also on the ADN of the epithelial cells from the crystalline. There are studies in the specialization literature, which shows that the UV radiation determines the changes in the structure of crystalline proteins and can modify the interactions of them, responsible for the maintenance of transparency of the crystalline in vivo [3].

The UV radiation in the optimal doses stimulates the development of young organisms and stops the apparition of the rachitic and the anemia, but the radiation that has a maximum of about λ=300 nm at certain dose provokes the cancer. The effect of this type of radiation on the plants also depends on the dose.

With the context of that mentioned, the necessity of exact appreciation of UV radiation dose by the UVimeter is evidently, the element of registration of radiation is the radiation UV photo-receiver. The great interest to the UV radiation receptors was increased considerably last years. This interest is thoroughly justified on the fact that the above mentioned spectral range in comparison with other spectral subranges, especially those of visible light, is insufficiently provided with the detectors of small dimensions.

Explanation and comparison of characteristics and parameters

Some models of detectors are proposed recently for the UV domain. The elaboration of portative apparatus is necessary for the extended application of UVimeter in the above mentioned ranges. For this elaboration, the application of semiconductor structures as the photo-receivers is necessary, because they posses all necessary qualities: are of small dimensions, resistant, and self supplying, posses the guaranteed protections [4]. For example, the authors of the paper [5] propose detectors with barrier on the surface of the epitaxial films *n-n+-GaP*. The measurement device of UV radiation UVR-21 is made on their base. The simplicity of production is mentioned in the paper as the quality of advantage and their exploitation. The researchers from the Ukraine SPhI of AS suggest photodiodes made on the base of halogenides of Cd for the commercialization, which can be applied for the registration of UV in different subranges of wavelengths [6]. We suggest different detectors for this spectral range on the base of layered multisulfides [7,8]. The technology of preparation of layered monocrystals is simply, but the method of appreciation of characteristics is already elaborated, being described in the papers [9-11]. For the bacterial subrange the photoresistors of the oxide and of cadmium aluminum sulfide are elaborated $(CdAl_2S(O_2))$ [12].

An analogical UVimeter with those mentioned was elaborated, built and implemented by the coworkers of State University of Medicine and Pharmacy "Nicolae Testemitanu" at the Otorhinolaryngology and the department of Human Physiology and biophysics, in collaboration with the Applied Physics Institute of Moldavan AS [7, 13-15].

One of the basic properties of semiconductor material used for the elaboration of UV radiation detectors is the large band gap (Eg≥3.0 eV) necessary for the exclusion or reducing to the minimum the sensitivity at visible and infrared radiation. This request is satisfied successfully by the compounds $Zn_3In_2S_6$ *(a)*, $Zn_3GaIn_6S_6$ *(b)*, *and* $Zn_3AlIn_2S_6$ *(c)* that belong to the group of halogenides with the crystalline structure as the form of layers and have the energy bang gap equal to 3.05, 3.25 and 3.37 eV respectively [10, 14]. The photoreceivers are elaborated and built with the spectral characteristic as the rectangle shape (П), on the base of layered monocrystals, which have the high sensitivity in the limits of photons with the energy higher than the energy band gap $h\nu>E_g$. This property is characteristic for the named transition due to of small speed of recombination on the surface of these semiconductors. The process of elaboration and building of photoreceivers is described in the papers [13-16]. The above mentioned monocrystals were used in order to build the photoreceivers. The monocrystals present the mounts with the surface area S ≥ 100 mm^2, which are cleaved easily up to the thicknesses of 10÷500 μm.

The photodiodes with the surface barrier (SBS) – Shottky diodes were elaborated as the photosensitive structures which have the following principle advantages:

- high photosensitivity into a high spectral range of wavelengths;

- electrical current supply device is not necessary, because the photocurrent is generated on the base of radiation that is received;
- Lux – amperical characteristic is linear into a large interval of received flux;
- simple technology of fabrication.

The detailed study of SBS was performed with different contacts on the base of layered monocrystals $ZnIn_2S_4$ [9, 10]. The analysis of obtained results allowed the formulation of their performed characteristics.

The film of Pt with the thickness of 10-15 nm was used as the rectification contact with the uniform transparence in whole range of near UV. The layer of ITO serves as ohm contact (mixture of SnO_2 and In_2O_3). Both contacts were deposited on the crystallographic planes by the method of thermal vaporization into a vacuum (0001) situated on both surfaces with the thickness of 10-20 nm. The coplanar contacts were deposited in the case of the detector on the base of the compound $CdAl_2S(O_2)$.

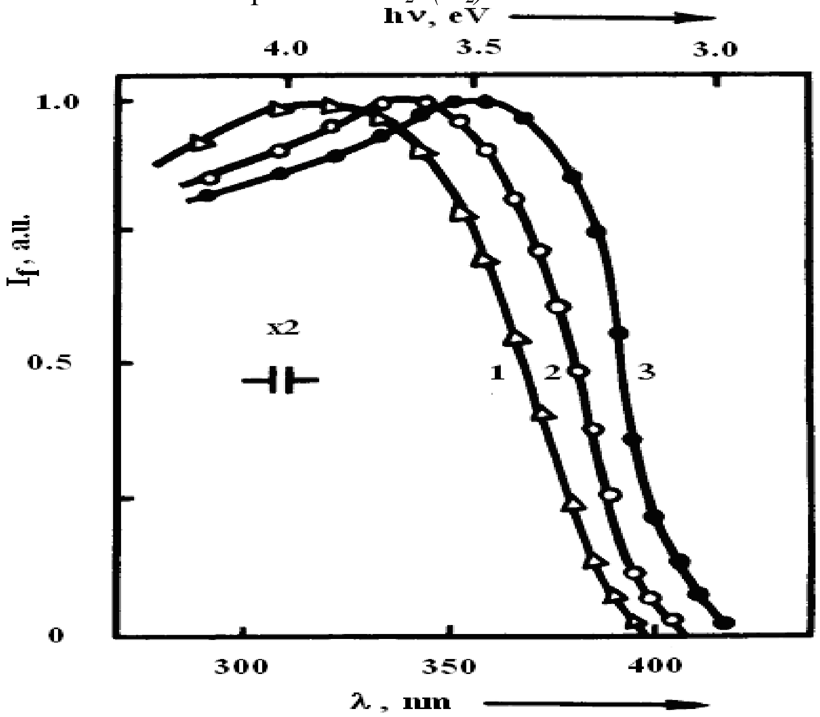

Figure 1. **The spectral dependence of photosignal of Shottky diodes on the base of the compounds Zn3InAlS6** (a), Zn3InGaS6 (b) and Zn3In2S6 (c) with the rectifying contact

The normalized spectral distribution of the photosignal of SBS made on the basis of multisulfides *a, b* and *c* is presented in Fig.1 (T = 300 K), which has large distribution and more pronounced removing in the range of short wavelengths in comparison with the photoconduction spectra. This is explained by the leakage of charge carriers in the contact region of the respective structure.

The value of forbidden band gap Eg of the compounds *a*, *b* and *c* increases in the named order, but the maximum of spectral distribution of the signal is removed in the direction of short waves of spectrum. In this case the SBS can be built, whose photosensitivity spectrum covers the entire near UV region, but with decreased relative sensitivity in the visible spectral range (λ=380÷400 nm).

The maximum of the open circuit voltage (V_{OC}) of the structure makes 400 – 600 meV and the rectification coefficient is 10^2 - 10^4. The maximum of V_{OC} spectrum is at 3.5, 3.7 and 3.2 eV for the SBS made of the compounds *a, b* and *c*, respectively.

The filters УФС – 2 and ЖС – 3 with the thickness of 0.1 cm are used in the real receivers for the limitation of spectral sensitivity and exclusion of non-desired band. The typical spectral characteristics are presented in the figure 2, but the main parameters of detectors are presented in the table 1.

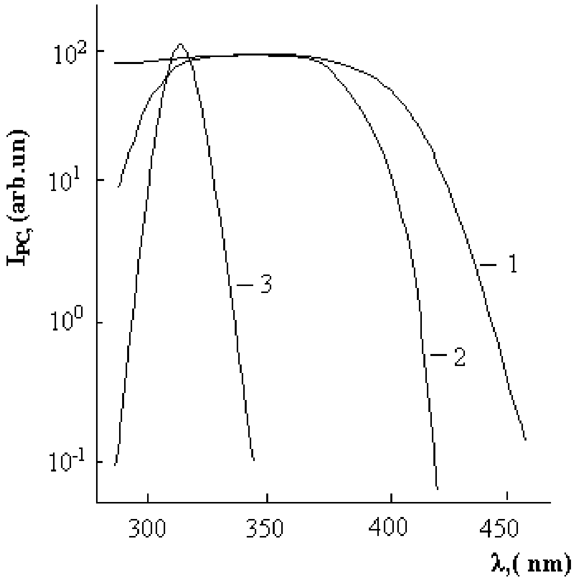

Figure 2. Spectral characteristics of photo signals of diodes:
(1) Pt-$Zn_3In_2S_6$ without filter;
(2) with filter;
(3) Pt-$Zn_3Ga(Al)InS_6$ with ЖС-3 filter

The research of the process of endurance of photodiodes exposed by UV radiation with high intensity (~$10^2 W/m^2$) and long ($3.6 \cdot 10^5$ s and more) proved that the structures with the contacts of gold or platinum do not indicate any omens of endurance. The application of these metals is preferable, because they influence little the cost of photoreceiver and for one device only 2 mg of Au or Pt are consummated, the duration of functioning of photoreceiver is enough long. The photoreceivers are applied for the measurement of absolute values of the UV fluxes radiation and work 4-5 years. The UVimeters and dosimeters are elaborated for UV radiation on their base. Both high stability and the simple system of registration of the signal provides for these devices the considerable advantages with respect to those built on the base of other compounds [15].

Table 1

Main parameters of detectors

Current sensitivity, $A \cdot cm^2/W$	$4 \cdot 10^{-4}$-$3 \cdot 10^{-3}$
Upper L – I_{PC} line limit, W/cm^2	10^{-4}-10^{-2}
Base resistance, Ω	10^5-$3 \cdot 10^6$
Photosignal duration, s	10^{-3}

The LAC of SBS diodes on the base of layered crystals is linear in the large limits of the intensities of UV radiation (up to 10^{-2} W/cm^2). It is evident that the UVimeters used for the measurement of smaller intensities will work long term. In order to increase the functioning term, the neutral homogenous filter for the near UV was used, which attenuate the intensity of about ×10, ×100 times. The filter represents a layer of Ni with the respectively thickness deposited on the support of quartz by the method of vaporization into a vacuum.

The elaborated photoreceivers on the base of Shottky diodes *Me-*$Zn_3In_2S_6$ have sensitivity in the fields of wavelengths 220÷400 nm. In order to reach some high performance of sensitivity in the field of spectral bands with the erythematic effect A, B and A+B, the cheap optical filters were used on the base of vitreous compounds. In order to register the radiation from the range A+B, the more convenient is the filter UFS - 2 with the thickness d=1 mm, but for the registration of the field A the system composed of filters UFS - 1 (d=1 mm) and SS-13 (d=2 mm) was used or the system composed by filters UFS – 1 (d=1 mm) and FS - 1 (d=2 mm). For the registration of the field B the filter UFS - 1 was chosen (d=1 mm) in the combination with GS - 3 (d=2 mm). Thus, for all three domains of erythematic radiation the filter UFS-2 must be used, it was installed in the interior of the transducer, but for the filter SS - 13 (FS - 1) and GS - 3 the possibility of dynamical installation was foreseen. For the commodities of the users the special construction [14] was elaborated that in front of transducer the obturator disc with three windows is installed (without filter and with filter GS-3 or SS-13 (FS-1)). Rotating the obturator disc, the fixing of one from those three windows in front of transducer takes place for the registration of radiation dose or the intensity in one of the above mentioned domains. It is evidently, that the standardization of electronic block was performed separately for each of those spectral domains (A, B, and C). The used crystals as is stated in the paper [17] have the high stability and, so that the elaborated photo receivers on their base will resist to the action of physical factors.

The spectra of elaborated photo resistors on the base of ceramic $CdAl_2O_4$ and mono crystals $CdAl_2S_4$ are presented in the figure 3 [12]. They cover the spectral range 220÷320 nm with high sensitivity at the wavelength of about 250 nm. The diodes have the high stability of functioning into a medium with a high degree of humidity, maintaining the absolute sensitivity of ~10^{-5} A·cm^2/W.

The compounds with the stoechiometrical vacancies, from which belong also those studied, have the high level of stability. Thus, we can look forward, that the devices will resist to considerable fluxes of ionized radiation. In order to study the stability of photodiodes at the action of radiation of radioactive nature, the structures $Pt\text{-}Zn_3In_2S_6\text{-}In$ were studied at the action of electronic flux with the energy about 40 keV. As the depth of penetrating of electrons by semitransparent electrode of *Pt.*

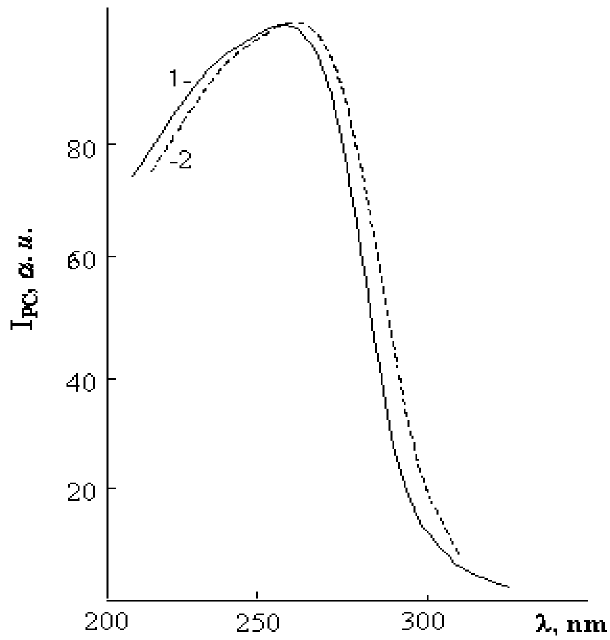

Figure 3. The typical spectra of the photoconduction
of ceramic $CdAl_2O_4$ (1) and $CdAl_2S_4$

in the monocrystals does not exceed some μm, the influence of ionization belongs to the lacked portion of the diode, but the space of the semiconductor with the thickness of about 10-20 μm is not affected practically to the influence of radiation. So that, in order to lead the influence, those parameters were chosen that determine the region of barrier: the spectral distribution of Voc, sensitivity, direct portion of volt-amperic characteristic at small voltages and indirect current. These parameters were measured for a set of diodes, before and after irradiation with the doses $6{\cdot}10^{16}$, 10^{17}, $6{\cdot}10^{17}$, 10^{18} el/cm^2. For first two doses the characteristics of diodes coincide with those initial. The change of the parameters of diodes are observed beginning with the dose $6{\cdot}10^{17}$ el/cm2 and is manifested by the changing of photosensitivity and maximum of Voc, the direct and indirect approximated increasing four times, the removing of the maximum position of photosignal to small energies of about 0.6 at the dose 10^{18} el/cm^2.

The combination of high values of photosensitivity and of stability creates the perspective that the multicomponent halogenides compounds can be used as the detectors for Roentgen radiation. The detectors of Roentgen radiation were built experimentally on the base of the compounds *a, b*, and *c* with the resistance at darkness 10^9 Ohm and high sensitivity in the range of quanta 1-10 keV. The factors of amplification, measured in the range of energies 2-7 keV exceed the value of 10^4 el/quantum. The time resolution does not exceed 10^{-9} s. These parameters allow the recommendation of named detectors for the diagnosis of laser plasma. We mention that on the base of above described detectors, using the experimental possibilities of the Institute of Applied Physics of AS of RM, the portative UVimeters were built and elaborated for the Republican Hospital of Children "Emilian Coțaga" where they were approved successfully. In conclusion we mention, that using the layered crystals of $Zn_3In_2S_6$, Zn_3GaInS_6 and Zn_3AlInS_6 , the detectors of UV radiation with high sensitivity were built and implemented in medicine at the portative devices for the measurement of intensity and radiation dose (practically all near UV). For example, we show the photographs of two devices built on the base of our elaborated diodes. (figures 4 and 5).

Figure 4. The device with logarithmical scale for the measurement of intensity values in the limits of 10^{-4}÷10 mW/cm^2 from the range of wavelengths 280÷400 nm. The supplying is 4.5 V

Figure 5. The measurement device with the digit display of UV radiation with the intensity in limits of values 10^{-4}÷2·10 mW/m^2 the spectral domains, nm: 280÷400, 320÷400, 320÷360; the dose - 0÷1.6·10^5 J/m^2. The current supplying – 220 V

These photo receivers with high stability at the irradiation and in accordance with it, they can found multiple practical applications, also for the creation of Roentgen radiation detectors on the base of the named semiconductor compounds and for the registration of density of electron fluxes.

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