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Anti-reflection coatings based on SnO_2, SiO_2, Si_3N_4 films for photodiodes operating in ultraviolet and visible spectral ranges

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Abstract. It is shown in this paper that tin dioxide coating is suitable to enhance sensitivity of photodiodes operating in the ultraviolet spectral range and based on zinc selenide and gallium phosphide. For these materials, the sensitivity values have been increased up to 0.12 and 0.2 A/W, respectively, in the maxima of their spectral characteristics. It is also shown that the film silicon nitride – silicon dioxide a bit better clarifies silicon photodiode, especially at the wavelength 700 nm. A gluing composition, in general, worsens transmission of films, and to greater extent transmission of the above film.

Keywords: anti-reflection coating, photodiode, ultraviolet, gallium phosphide, zinc selenide.

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1. Introduction

The expansion of the researches that concern ultraviolet (UV) radiation of both artificial and natural origin predetermines development and improvement of the proper optical sensors, in particular, it is essential for photodiodes sensitive in the UV spectral range. The spectral range on Earth's surface covers a range between 200 to 380 nm, which imposes certain restrictions on these sensors.

One factor that remarkably contributes to the sensitivity of photodiodes is the presence of anti-reflection (AR) coating that reduces losses in the intensity of light reaching the light-sensitive layer.

To enhance the photodiode sensitivity in UV, we use a nanosized layer of SnO_2 [1]. It can serve also as an active electrode optically transparent within the range 350 to 1100 nm. High transparency of SnO_2 films in the UV region is related to the high value of the forbidden band (E_g ~3.8 eV). Besides, refraction of this layer (SnO_2) ideally fits for creation of AR coatings. Its transmission coefficient achieves 9.6% at the layer thickness 54.4 nm for the wavelength 435 nm.

On the other hand, no less urgent is the task of increasing the sensitivity of silicon $p-i-n$ photodiodes. These are intended for connection in the optoelectronic couple "scintillator-photodiode" that is the optoelectronic detector for registration of gamma-, X-ray radiation and other high-power radiations. In this couple, it is necessary to provide maximum transmittance of luminescent radiation from the scintillator to photodiode. That is the main reason why the AR coatings have an important significance in improving the efficiency of the above detectors.

Thus, there were two main purposes of this work. The first one was studying the spectral characteristics of photodiodes based on zinc selenide (ZnSe) and gallium phosphide (GaP). The second one was to rise the sensitivity of silicon $p-i-n$ photodiodes that are intended for connection in the optoelectronic couple scintillator-photodiode by creation of AR coating that was used for covering these structures and investigated.

2. Test photodiode structures for studying the AR coatings operating in the UV spectral range

The photodiodes that are intended for functioning in the UV spectral range are made of different materials. In our work, we have considered the AR coatings intended to improve the sensitivity of photodiodes based on zinc selenide and gallium phosphide $[2-4]$.

The layers of SnO_2 with different thicknesses were deposited on their surface in laboratory conditions.

In the first case, our test structures were ZnSe photodiodes with the Schottky barrier. In the second case, we used surface-barrier photodiodes based on GaP [5].

Photodiodes based on ZnSe substrates of the *n*-type doped with tellurium or oxygen and possessing the thickness 1 mm contained an extremely thin barrier layer of nickel with the thickness that was no higher than 10 nm. On the thin barrier layer of nickel, by using the method of sputtering we deposited the AR layer of mixture containing tin dioxide (SnO_2) and indium(III) oxide (In_2O_3), or layer of tin dioxide (SnO_2) doped with fluorine. Formed at the periphery of the crystal was the additional contact layer of nickel with a thickness not less than 0.2 μm, the purpose of which was to provide the electric contact to the nickel barrier layer. The distance between the layers of nickel and edge of the zinc selenide crystal was not less than 10–50 μm. Formed from the back of the zinc selenide crystal was the layer of indium with a thickness from 1 to 20 μm [6] that had to provide the second electric contact.

Photodiodes based on gallium phosphide were made on epitaxial $n - n^+$ structures with the concentration of charge carriers about $10^{16}\,\mathrm{cm}^{-3}$. The thickness of epitaxial layer was within the limits of 10 to 15 μm. The barrier contact on the surface of epitaxial layer was created using deposition of thin conducting layers of tin dioxide (SnO_2), and indium(III) oxide (In_2O_3) or their mixture (ITO) [7].

We used alcohol solution of tin(II) chloride ($SnCl_2$) with addition of fluorine ammonium. The ohmic contact was created by smelting inside the In-Ni alloy in a vacuum (or in the atmosphere of hydrogen) at a temperature about 550-600 °C. In order to avoid an undesirable contamination, during the smelting the plates were laid by their front side on a flat surface. Before deposition of tin dioxide layer, the plate surface was processed in solution of bromine in dimethylformamide with the subsequent washing in alcohol. As a contact layer for tin dioxide (SnO_2), the deposited nickel was used. Separation of photosensitive elements and contact layers was performed using the standard methods of photolithography. Connection of the contacts was carried out by soldering the copper tin-plated leads to the contact layers. When using the ultrasonic welding, we used the variant of structure in which the contact layer of metallization partially covered the protective layer of silicon dioxide.

Spectral characteristics of the current monochromatic sensitivity for these UV photodiodes are represented in Fig. 1.

Curves *1*, *2*, *3* – spectral characteristics of the sensitivity typical for photodiode based on ZnSe; *1* – without an AR layer; *2* – with AR layer for the wavelength 250 nm; *3* – with AR layer for the wavelength 400 nm. Curves *4*, *5* are spectral characteristics of the current monochromatic sensitivity of photodiodes based on GaP. *4* – AR wavelength 310 nm; *5* – AR layer is absent.

One can see in the picture that AR coating with SnO_2 increases the sensitivity of UV photodiodes by 20 to 40% depending on the wavelength.

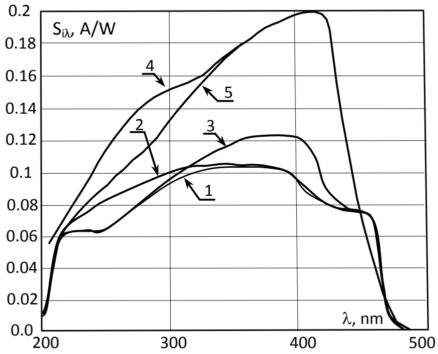

Fig. 1. Spectral characteristics of the current monochromatic sensitivity for UV photodiodes based on zinc selenide and gallium phosphide. *1*, *2*, *3* – spectral characteristics of the sensitivity typical for photodiode based on ZnSe: *1* – without an AR layer; *2* – with AR layer for the wavelength 250 nm; *3* – with AR layer for the wavelength 400 nm. Curves *4*, *5* are spectral characteristics of the current monochromatic sensitivity of photodiodes based on GaP. *4* – AR layer for the wavelength 310 nm; *5* – AR layer is absent.

Thus, it is shown that the application of AR coatings made of SnO_2 film to rise the sensitivity of photodiodes that are sensitive in the UV spectral range and based on zinc selenide as well as gallium phosphide is a promising way. This technical decision is used for elaboration of specialized photodiodes for acquisition in dosimeters of UV radiation “Tenzor-53” and radiometers of UV radiation “Tenzor-31” that are intended for the research of natural (sun) and artificial UV radiation [8]. Application of the described AR coatings allowed us to increase the sensitivity of photodiodes based on GaP in the maximum of their spectral characteristic (~400 nm) to 0.2 A/W, and for photodiodes based on ZnSe in their spectral maximum (~380 nm) to 0.12 A/W. These results allowed us to significantly increase the dynamic range of dosimetric devices. Now the dynamic range comprises 10^{-4} to 2×10^2 W/m^2 [9].

3. Testing the photodiode structures for studying the AR coatings on silicon *p – i – n* photodiodes that operate in optoelectronic couples scintillator-photodiode

The second direction of our work is aimed at increase in the sensitivity of silicon $p - i - n$ photodiodes used in optoelectronic couples scintillator-photodiode [2, 10]. In this case, it is necessary to provide maximal transmission of luminescence radiation through the AR layer to a photodiode. This kind of couples operates as the optoelectronic detector for registration of gamma- or X-ray radiation and other high-power radiations. That’s why, the AR coating is rather important to increase the efficiency of these detectors.

For scintillators with the short-wave luminescence radiation, for example NaJ(TI) and LSO, which radiate in the range of 410-420 nm, the usage of a silicon photodiode without increasing its sensitivity in UV region is impossible.

To provide maximal transmittance of the intrinsic radiation spectrum of scintillators that considerably depends on AR coating on the surface of photosensitive elements is a very important stage. In this exact work, computation of spectral characteristics for light transmission and absorption is performed depending on the thickness and materials of the layers of photodiode AR coatings that are formed in the process of making the photodiode crystal.

We carried out selection and calculations of parameters of AR coatings on $p-i-n$ photodiodes that are based on silicon with the usage of such scintillators as: CsJ(TI) (λ = 550 nm); ZnSe (λ = 610 nm); NaJ(TI) (λ = 410 nm); LSO (λ = 420 nm).

Shown in Fig. 2 is the model of the optical transition area between the scintillator and photodiode, which is used to calculate the spectral characteristics of transmission and absorption. In this model, widespread layers of SiO_2 and Si_3N_4 are used.

Parameters of AR coatings of SiO_2 and (SiO_2+Si_3N_4) were calculated using the Abel matrix method. This model is used for computation of the spectral characteristics of light transmission and absorption. The indexes of refraction for materials used in this computation are shown below:

optical glue – 1.45; SiO_2 – 1.459; Si_3N_4 – 1.968; CsJ(Tl) – 1.79; NaJ(Tl) and LSO – 1.85; ZnSe – 2.55.

The wavelengths that are radiated by scintillators are 420 nm (NaJ(Tl) and LSO), 550 nm (CsJ(Tl)), 610…630 nm (ZnSe). The coefficient of transparency that was calculated for these wavelengths exceeded the value 0.9. Current monochromatic sensitivity of silicon $p-i-n$ photodiodes at the wavelength 420 nm with this AR coating gets better more than by 10%.

Shown in Fig. 3 as illustration are the structure of a $p-i-n$ photodiode (a), and the structure of transitional region between the scintillator and photodiode (b).

The results of modeling the behavior of the transparency of single-layer and double-layer AR coatings are given below in Figs 4 and 5.

Fig. 4 illustrates the dependences of the light transmission coefficient T_c on the radiation wavelength λ (single-layer coating by the film of SiO_2 with the thickness 180 nm) for the sample without glue (a) and for the sample with the thickness of glue 20 μm.

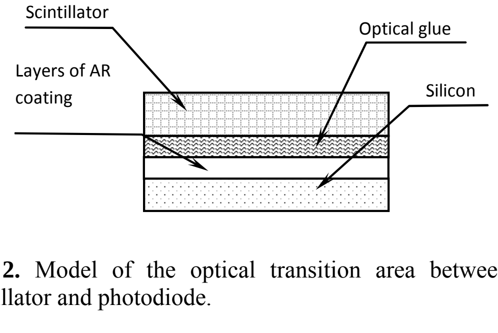

Fig. 2. Model of the optical transition area between the scintillator and photodiode.

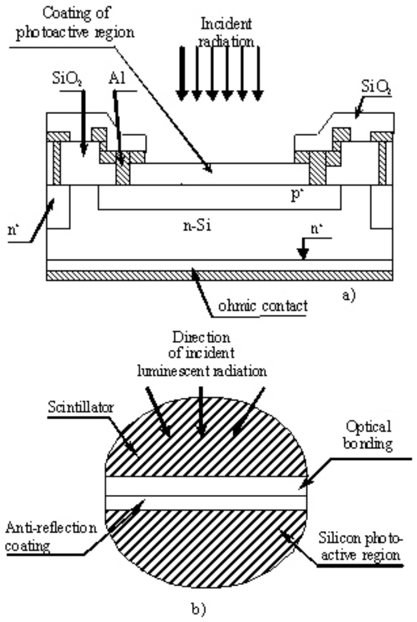

Fig. 3. Structure of a *p-i-n* photodiode (a) and transition area between the scintillator and photodiode (b).

The spectral dependence of the transparency shown in Fig. 4 has a maximum at the wavelength 540–550 nm and can be used in selecting the parameters of AR coatings for a photodiode in the optocouple with scintillator that has the emission wavelength λ = 540–550 nm, for example CsJ(Tl).

The results of computations shown in Figs 4 and 5 allow to determine parameters of technological films SiO_2 and Si_3N_4, which are needed to achieve the maximal transparency of photodiode coating and maximal possible value of the sensitivity inherent to a silicon $p-i-n$ photodiode for the used wavelength, i.e., for certain material of the scintillator.

As seen from the curves in Fig. 4, the transmission coefficient of the film with silicon dioxide possessing the thickness 180 nm has a maximum value 0.85 near λ = 550 nm. From the curves in Fig. 4, it is also obvious that the transparency of SiO_2 film with the thickness 180 nm and the same film with a layer of glue (thickness of 20 μm) are different. In the second case, the transmission T_c oscillates around the average value, with a maximum value in the curve reduced by about 5% as compared to the first option, and the value in minimum increases (also about 5%). This behavior is the calculated curve for the second case that is apparently related with numerical calculation for different film thicknesses of SiO_2 and glue (difference in thickness of almost two orders of magnitude).

Spectral dependences of the light transmission for double-layer AR coating SiO_2+Si_3N_4 shown in Fig. 5 reach a maximum 98% at the wavelength 420 nm, which is significantly higher than the transmission of coatings in the single-layer case. Thus, the thicknesses of SiO_2 and Si_3N_4 layers are chosen in such a manner that they have the maximum transmission for “blue” scintillators, for example, NaJ(Tl), LSO and others.

The results of this research allow us to make calculations of optical parameters of construction of the photodiode operating in a system of scintillator-photodiode, as well as other designs, including photodiodes that are used for measuring in ultraviolet and visible spectral ranges. All these computations were produced on the basis of the elaborated program.

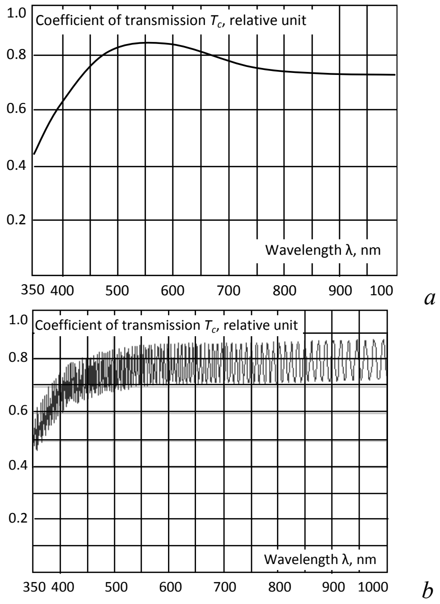

Fig. 4. Dependences of the light transmission coefficient T_c on the radiation wavelength λ (single-layer coating by the film of SiO_2 with the thickness 180 nm) for the sample without glue (a) and for the sample with the thickness of glue 20 μm (b).

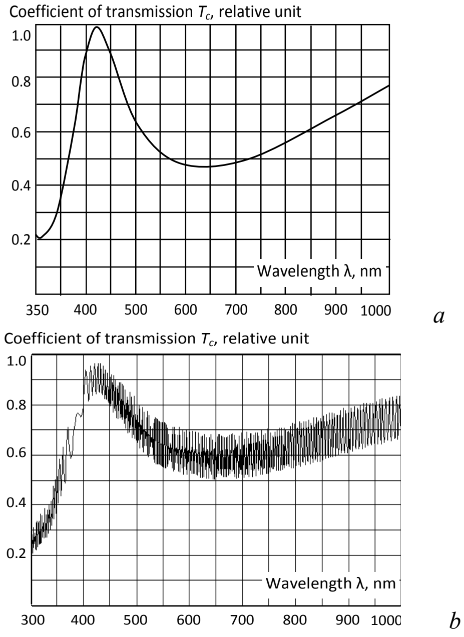

Fig. 5. Spectral dependences of the light transmission for double-layer AR coating SiO_2+Si_3N_4. Thicknesses of the films: 136 nm for SiO_2, 60 nm for Si_3N_4; (a) without glue; (b) the thickness of glue layer 20 μm.

4. Conclusions

1. AR coatings that are made of the film of tin dioxide have been explored. It has been shown that these coatings conduce to the growth of the sensitivity of photodiodes based on zinc selenide and gallium phosphide that are sensitive in the UV spectral range to 0.12 A/W and 0.2 A/W, accordingly, in the maximum of spectral sensitivity characteristic.

2. Using the specialized program, the transmission coefficients of AR coatings of silicon dioxide and silicon nitride have been analyzed both with gluing composition and without it. It has been shown that film of silicon nitride – silicon dioxide rises the sensitivity of photodiode not less than by 10–15%.

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