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Photoelectric properties of amorphous Ga_2O_3, films doped with phosphorus and selenium

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Received March 24, 2025
Revised September 23, 2025
Accepted September 25, 2025

Data on the influence of selenium and phosphorus on the electrical and photoelectric characteristics of gallium oxide films are presented. Planar metal$-Ga_2O_3-$metal resistive structures were fabricated on sapphire substrates using RF magnetron sputtering, with a distance of 1 mm between Pt electrodes. The effects of Se, P, and a mixture of Se + P on the dark currents and photocurrents of the samples under irradiation with wavelengths of $\lambda = 254$ and 808 nm were investigated.

Keywords: gallium oxide, doping, sapphire substrate, UV radiation.

DOI: 10.61011/TP.2026.01.62852.45-25

Introduction

An increased interest to using wide-band semiconductors in various-purpose electronics is due to their unique properties. Designs based on these materials, including gallium oxide, are especially promising for future power electronics. Achievements in this field can be used in some spheres, including operation of electric cars, data processing centers, consumer electronics, a space telecommunications sector. Up to now, there are various technologies for producing high-quality single crystals and thin Ga_2O_3 layers and methods of varying conduction within several orders $10^{16}-10^{20}\,cm^{-3}$ are found[1–6]. One of the essential factors that restrain wide application of gallium oxide for practical designs is that there is no material of p-type conduction, thereby preventing designing bipolar appliances. This problem is solved by doping Ga_2O_3 with various dopants in order to produce fine acceptors with a concentration that is enough to compensate donor centers, which are created in gallium oxide both due to vacancies of oxygen atoms as well as due to uncontrolled dopants. Sometimes, published results on a behavior of dopants in gallium oxide turn out to be contradictory. Thus, it is stated in the study [7] that doping Ga_2O_3 with selenium can provide a transition to hole conduction. It is shown by special calculations that when selenium is introduced into gallium oxide, a solid solution β-$Ga_2(O_{1-x}Se_x)_3$ is formed. A conduction band is almost unchanged; the main changes are observed in a valence band. In indicates a significant role of *p*-orbitals of selenium in forming a band structure of the valence band of the solid solution. At the same time, using a method of a density functional theory, Song with colleagues showed that in the β-Ga_2O_3 lattice selenium atoms could replace both oxygen ions as well as gallium ions [8]. Taking into account the same number of valence electrons in atoms of oxygen and selenium, a difference in sizes of their ionic radii and high electronegativity of the oxygen atoms, it has been concluded that the selenium atoms in gallium oxide can be only effective donors. The studies [9,10] analyze the influence of implantation of phosphorus ions on electrical characteristics of β-Ga_2O_3 epitaxial layers grown by MOCVD on sapphire substrates. It is shown that the type of conduction of gallium oxide can be changed only when using mid and high doses of implantation of the phosphorous ions. In most cases, the behavior of dopants in gallium oxide is studied by calculation methods and these studies are not always experimentally confirmed. In the present study, we present experimental results of the studies of the influence of selenium and phosphorus on the electrical characteristics and sensitivity to UV and long-wavelength radiation of planar resistive structures based on Ga_2O_3 films.

1. Experimental procedure

The experiment was on samples that were metal$-Ga_2O_3-$metal (M$-Ga_2O_3-$M) resistive structures formed on the sapphire substrates. The gallium oxide film of the thickness of 150–200 nm was applied by HF-magnetron sputtering. A mode of application of the Ga_2O_3 film to the sapphire substrate is described in the study [11]. In order to study the influence of doping, the sapphire plates with the applied Ga_2O_3 films were placed in separate quartz tubes with subsequent depressurization to a vacuum level of 10^{-6} Pa and sealing. In addition to the samples, the quartz tubes also included powders of the dopant: phosphorous of the weight of 0.425 g; selenium of 0.505 g; a mixture of selenium and phosphorous of 0.505

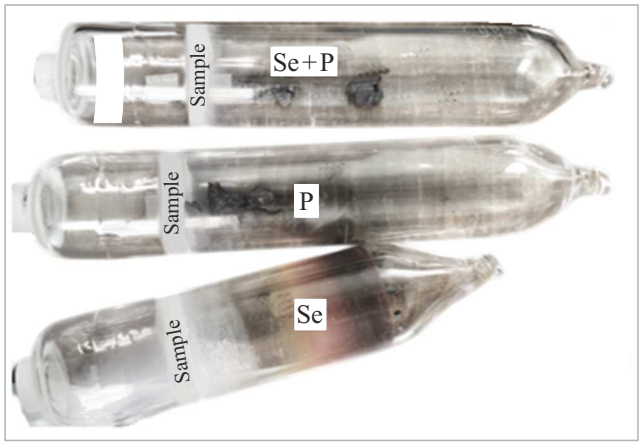

Figure 1. Photos of tubes with the doped samples.

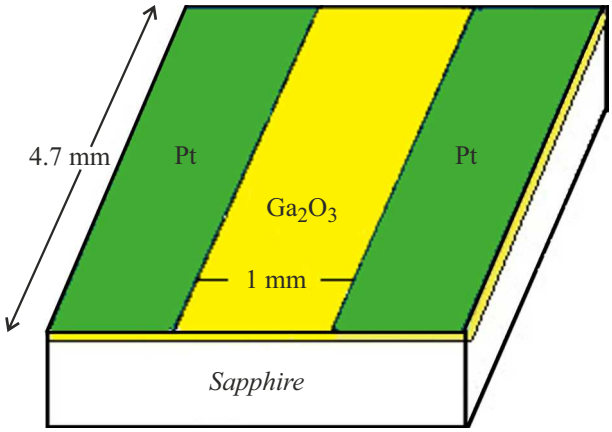

Figure 2. Appearance of one of the samples.

and 0.42 g, respectively (Fig. 1). A granule size of the powders of phosphorous and selenium was 0.1 and 2 mm, respectively. The sealed quartz tubes were transferred into an oven, whose temperature was raised to 600 °C for 12 h. Pressure in the tubes during doping was determined by vapor of an evaporated dopant. At the temperature of 600 °C the plates were held at 100 h and left to be cooled to the room temperature for 24 h.

A depth of diffusion of phosphorous and selenium into the Ga_2O_3 film was determined by a method of secondary ion mass-spectroscopy (GD-Profiler HR) and is given in the study [12]. Selenium is uniformly distributed in the gallium oxide film and its concentration is much lower as compared to phosphorous. Sample manufacturing was finished by template sputtering of Pt-electrodes to an oxide film surface. A distance between the platinum contacts is 1 mm, and a length of the electrodes is 4.7 mm (Fig. 2). It was previously shown that the gallium oxide films produced on the sapphire substrates by HF-magnetron sputtering and unheated at the high temperature turned out to be amorphous [13].

Dark current-voltage characteristics (I-V curves) and the I-V curves under radiation were studied at the room temperature within the voltage range $0 \le V \le \pm 100$ V using a Keithley 2636A sourcemeter. A krypton-fluorine lamp LEAC-280L with a 254 nm filter was used as a UV radiation source. Incident intensity of radiation was $4.7 \cdot 10^{-2}$ W/cm^2. The photovoltaic characteristics in the long-wavelength range were measuring using a laser with $\lambda = 808$ nm and power of 500 mW with incident intensity of 16 W/cm^2.

2. Experimental results and their discussion

The dark I-V curves of the studied samples are described by a linear dependence of the current on voltage and do not depend on voltage polarity. In the M–Ga_2O_3–M structures with the selenium-doped oxide film (Ga_2O_3:Se), the dark currents I_D either turn out to be less than similar magnitudes for the samples based on the undoped film or have the same values (see Fig. 3, the insert).

Doping the gallium oxide films with phosphorous results in an increase of the dark currents by an order as compared to I_D for the undoped structures. Introduction of selenium makes almost no impact on the dark current, while with joint doping with phosphorous and selenium the currents insignificantly increase (Fig. 3). Table provides values of the dark currents at voltage of 100 V.

Fig. 4 shows the I-V curves of the structures without impact by radiation with $\lambda = 254$ nm and with it. The highest values of illumination currents (I_L) were obtained for the structures with the gallium oxide film doped with phosphorous. The values of the currents I_L at voltage of 100 V and the ratio I_L/I_D are provided in Table.

The ratios I_L/I_D (contrast) in the structures Pt–Ga_2O_3–Pt and Pt–Ga_2O_3:Se–Pt do not practically depend on voltage, whereas in the samples with the oxide film containing phosphorous the ratio I_L/I_D increases with

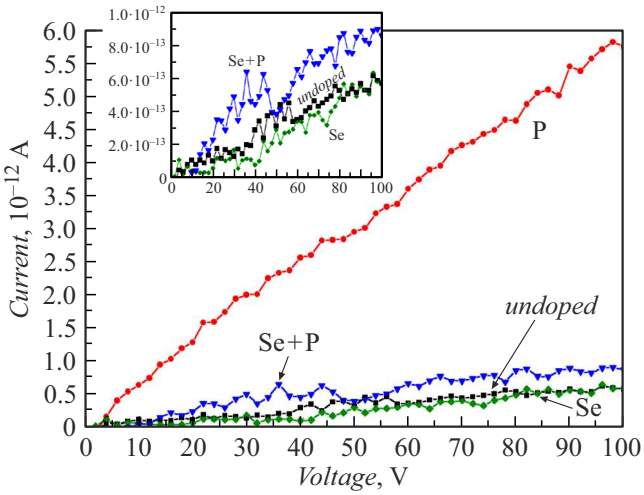

Figure 3. I-V curves of the structures without UV radiation; the insert in a more detailed scale shows the I-V curves for the samples with an undoped gallium oxide film, a Se-doped one and one doped with the Se + P mixture.

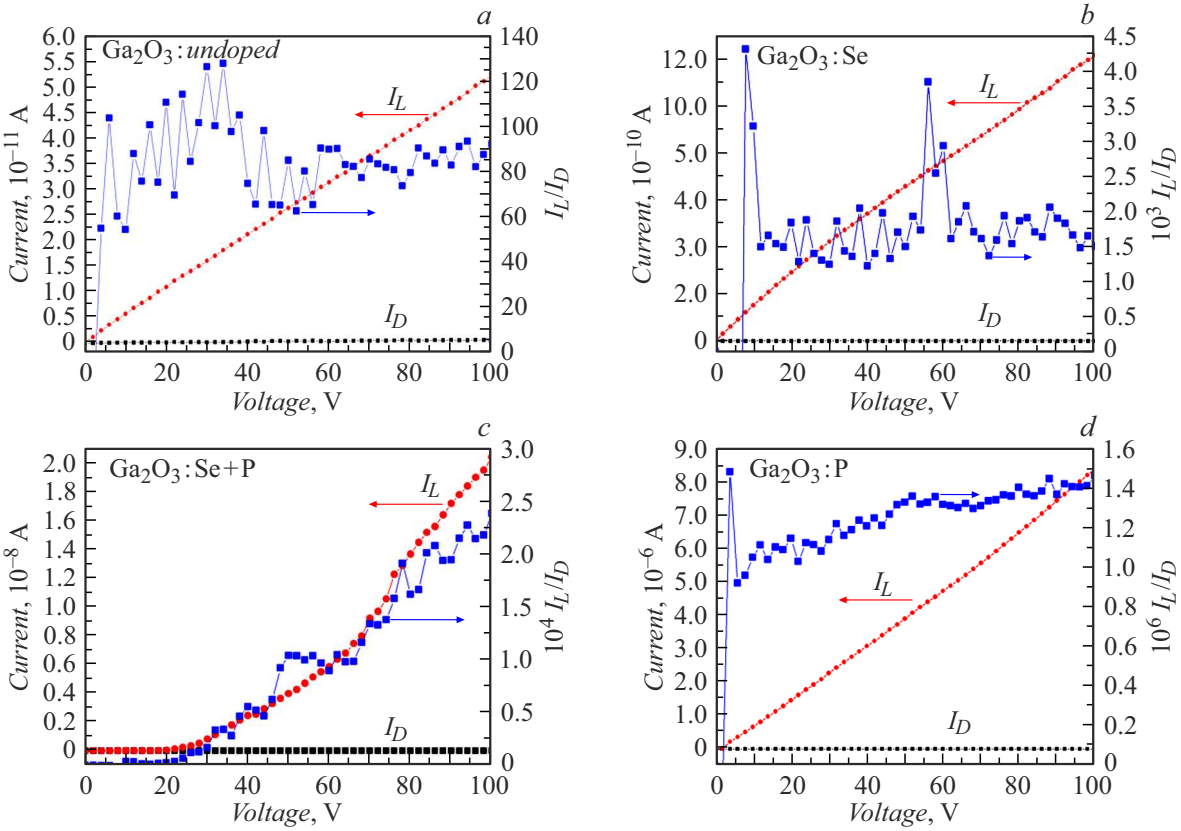

Figure 4. Dark and light I-V curves of the samples with the undoped gallium oxide film (*a*) and the doped gallium oxide films (*b–d*); $\lambda = 254$ nm; I_D — the dark current; I_L — the current under radiation.

Some characteristics of the structures Pt−Ga_2CO_3−Pt

Sample	I_D, A (100 V)	I_L, A (100 V)	I_L/I_D	R, A/W	D^*, Jones
Ga_2O_3	$5.7 \cdot 10^{-13}$	$5.2 \cdot 10^{-11}$	$9.1 \cdot 10^{1}$	$2.4 \cdot 10^{-7}$	$5.6 \cdot 10^{8}$
Ga_2O_3:Se	$5.8 \cdot 10^{-13}$	$1.2 \cdot 10^{-9}$	$7.6 \cdot 10^{3}$	$5.5 \cdot 10^{-6}$	$1.3 \cdot 10^{10}$
Ga_2O_3:Se + P	$8.6 \cdot 10^{-13}$	$2.0 \cdot 10^{-8}$	$2.3 \cdot 10^{4}$	$9.1 \cdot 10^{-5}$	$1.7 \cdot 10^{11}$
Ga_2O_3:P	$5.7 \cdot 10^{-12}$	$8.3 \cdot 10^{-6}$	$1.5 \cdot 10^{6}$	$4.0 \cdot 10^{-2}$	$3.1 \cdot 10^{13}$

an increase of voltage (Fig. 4, *c, d*). In the structures with the Ga_2O_3:P film a value of the response R increases by five orders as compared to the undoped samples, whereas in the samples with the Ga_2O_3:Se film the response increases by one order (see Table). Thus, doping with phosphorous can be considered to be a method of increasing sensitivity of the gallium oxide films produced by the simplest method to UV radiation.

Despite the large dark currents as compared to the other samples, the Pt−Ga_2O_3:P−Pt structures exhibit maximum values of the response R and effective detectability D^* (see Table). The values R and D^* were calculated by the formulas provided in the studies [14–16]. Joint introduction of selenium and phosphorous into the oxide film reduces the influence of P on UV sensitivity of the studied samples. The ratios I_L/I_D increase with an increase of voltage only in the samples with the gallium oxide films containing phosphorous (Fig. 4, *c, d*). After switching off UV, all the structures practically did not include residual photoconductivity.

Doping affects the time characteristics of the studied samples. Introduction of the dopant results in formation of additional defects in the oxide film and capture of electrons on them. Under UV radiation, a photocurrent is cased by the transition of electrons from the valence band (E_v) into the conduction band (E_c) as well as generation of electrons from trap centers in E_c. Fig. 5 shows the curves of a dependence of current variation (I) in time (t) when switching on/off the radiation source with $\lambda = 254$ nm at the structure voltage of 20 V.

It can be concluded from comparing the curves in Fig. 5 that the structures based on the doped gallium oxide films

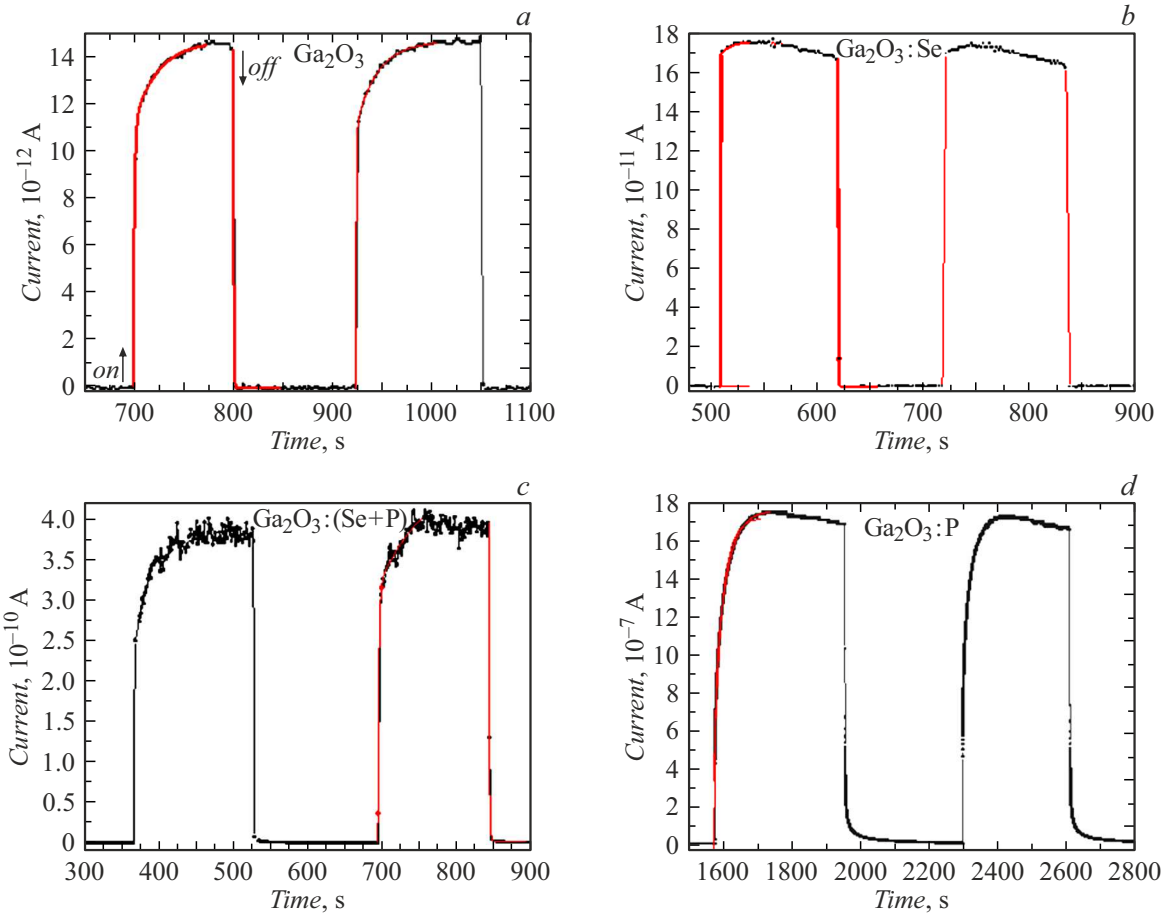

Figure 5. Time profiles of current variation when switching on/off radiation with $\lambda = 254$ nm; voltage on structure — 20 V.

exhibit a faster increase of the photocurrent when switching on UV as compared to the samples with the Ga_2O_3 films. The structures with the $Ga_2O_3:P$ film, which exhibit a maximum response, have longer time of photocurrent reduction after switching off UV radiation.

The influence of phosphorous on the properties of the metal$-Ga_2O_3:P-$ can be explained taking into account that P_2O_5 is a good glass former [17]. It is assumed that interaction of phosphorous with oxygen results in an increase of a concentration of deep oxygen vacancies V_0 in the gallium oxide lattice. Under ultraviolet impact, oxygen vacancies are ionized, ions V_0^{2+} are created and the conduction band originates an additional contribution to the structure response in addition to interband generation [18,19]. Presence of a potential barrier when electrons are captured to these levels during recombination results in an increase of current relaxation time after switching off radiation [18].

An assumption about a large concentration of traps in $Ga_2O_3:P$ is confirmed by data obtained when the structure is affected by radiation with $\lambda = 808$ nm (1.53 eV). Sensitivity of the structures to long-wavelength radiation is explained by presence of the trap centers in the band gap of gallium oxide. Differences between the dark currents and currents in presence of radiation with $\lambda = 808$ nm are determined by the introduced dopant (Fig. 6).

The samples with the undoped gallium oxide made almost no reaction to radiation with $\lambda = 808$ nm within the voltage range from 0 to 100 V. In the structures with the selenium-containing films, the ratios I_L/I_D were increasing when $V \geq 70$ V (Fig. 6, *b, c*). The largest influence of long-wavelength radiation was observed in the samples with the $Ga_2O_3:P$ film. But, unlike the behavior in the UV ranges, the ratios I_L/I_D were decreasing with the increase of voltage at the structures (Fig. 5, *d*). The effect is explained by an increase of dark currents in these structures as compared to the undoped samples, about which it is said above (see Table). At the same time, it is known that in the visible and near-IR ranges gallium oxide exhibits a high transmittance coefficient and absorption at the wavelength of $\lambda = 808$ nm turns out to be low.

It is concluded based on the obtained data that unlike conclusions made in the studies [9,10] phosphorous in Ga_2O_3 creates a high concentration of the donor centers. As a result, the dark current in the structures with the $Ga_2O_3:P$ film is by four orders higher as compared to I_D in the samples with the undoped gallium oxide film. The high values of the photocurrent when $\lambda = 254$ nm seem to be caused not

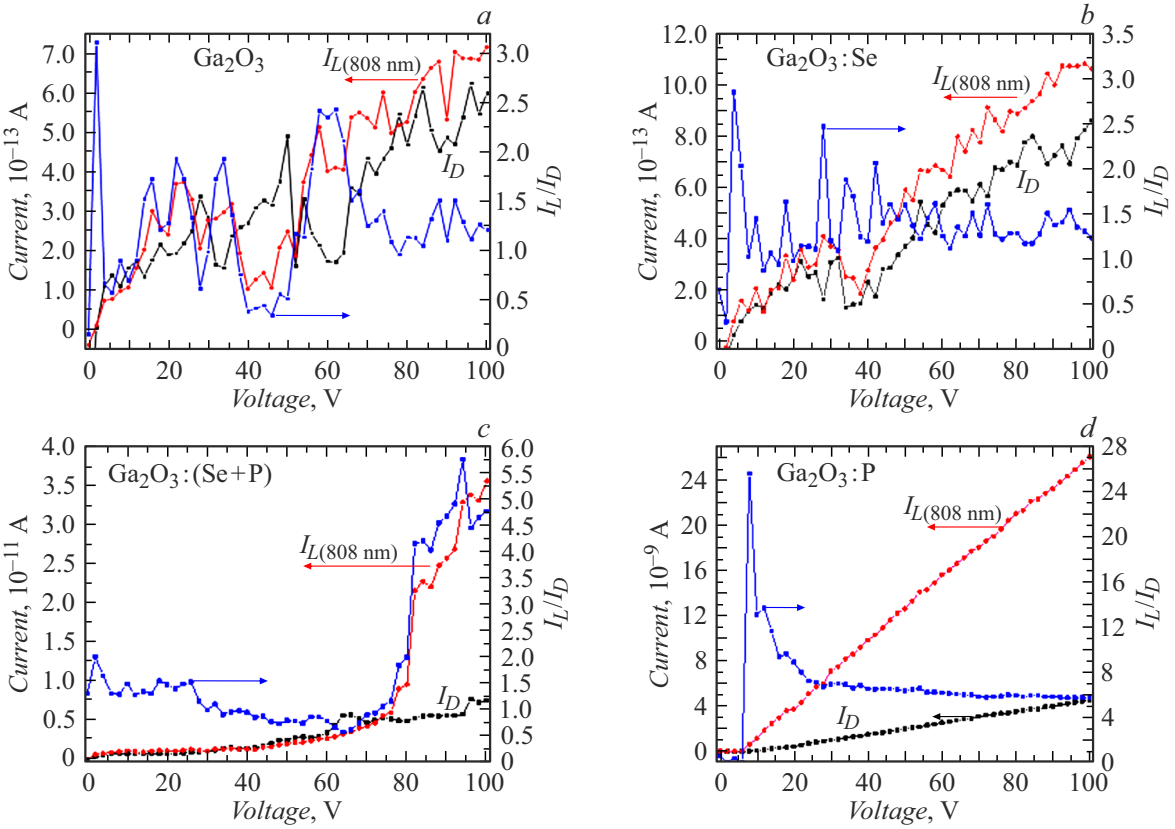

Figure 6. Dark and light I-V curves of the samples with the undoped gallium oxide film (*a*) and the doped gallium oxide films (*b*–*d*); $\lambda = 808$ nm.

only by the transition of electrons from the valence band into the conduction band E_c, but by generation of electrons from the trap centers in E_c as well. Taking into account a complex structure of the Ga_2O_3 crystal lattice we assume that the phosphorous atoms can interact with oxygen both in an octahedral and a tetrahedral configuration, which can result in origination of defects with various energy levels. Under impact of radiation with $\lambda = 808$ nm, the photocurrent originates in the metal$-Ga_2O_3$:P$-$metal structures due to excitation of electrons from the trap centers localized at the energy levels $E_t \leq E_c$ — 1.5 eV. Taking into account calculation data specified in the study [9], we assume that the Ga_2O_3:P films can form local centers with activation energies exceeding E_c — 1.5 eV. In addition to interband generation, excitation of electrons from these traps provides an additional photocurrent in the UV range.

Conclusion

We have compared the electrical and photovoltaic characteristics of the gallium oxide films undoped and doped with selenium and phosphorous. Selenium doping practically does not change the dark currents of the metal$-Ga_2O_3-$metal structures and by two orders increases sensitivity to radiation with $\lambda = 254$ nm as compared to the undoped gallium oxide layers. In the structures with the Ga_2O_3:P films sensitivity to radiation with $\lambda = 254$ nm is by 4–5 orders higher in relation to the thin Ga_2O_3 layers. Doping gallium oxide with phosphorous can be considered to be the method of increasing sensitivity of the gallium oxide films produced by HF-magnetron sputtering to UV radiation.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by M.Shevelev