View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by Tomsk State University Repository

ISSN 1063-7826, Semiconductors, 2015, Vol. 49, No. 3, pp. 345–351. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © V.M. Kalygina, V.V. Vishnikina, Yu.S. Petrova, I.A. Prudaev, T.M. Yaskevich, 2015, published in Fizika i Tekhnika Poluprovodnikov, 2015, Vol. 49, No. 3, pp. 357–363.

SEMICONDUCTOR STRUCTURES, LOW-DIMENSIONAL SYSTEMS, AND QUANTUM PHENOMENA

Photoelectric Characteristics of Metal–Ga_2O_3–GaAs Structures

V. M. Kalygina^, V. V. Vishnikina, Yu. S. Petrova, I. A. Prudaev, and T. M. Yaskevich

National Research Tomsk State University, Tomsk, 634050 Russia

^e-mail: Kalygina@ngs.ru

Submitted March 27, 2014; accepted for publication April 28, 2014

Abstract—We investigate the effect of thermal annealing in argon and of oxygen plasma processing on the photoelectric properties of GaAs–Ga_2O_3–Me structures. Gallium-oxide films are fabricated by photostimulated electrochemical oxidation of epitaxial gallium-arsenide layers with *n*-type conductivity. The as-deposited films were amorphous, but their processing in oxygen plasma led to the nucleation of β-Ga_2O_3 crystallites. The unannealed films are nontransparent in the visible and ultraviolet (UV) ranges and there is no photocurrent in structures based on them. After annealing at 900°C for 30 min, the gallium-oxide films contain only β-Ga_2O_3 crystallites and become transparent. Under illumination of the Ga_2O_3–GaAs structures with visible light, the photocurrent appears. This effect can be attributed to radiation absorption in GaAs. The photocurrent and its voltage dependence are determined by the time of exposure to the oxygen plasma. In the UV range, the sensitivity of the structures increases with decreasing radiation wavelength, starting at $\lambda \leq$ 230 nm. This is due to absorption in the Ga_2O_3 film. Reduction in the structure sensitivity with an increase in the time of exposure to oxygen plasma can be caused by the incorporation of defects both at the Ga_2O_3–GaAs interface and in the Ga_2O_3 film.

DOI: 10.1134/S1063782615030100

1. INTRODUCTION

Gallium oxide Ga_2O_3 belongs to a large group of metal-oxide compounds widely used in electronic and optoelectronic device engineering. Ga_2O_3 can be in any of the five phases α, β, γ, δ, or ε, but the first two phases, α and β, are the most interesting for fundamental research and applications. In combination with Al_2O_3 or CdGaO layers, gallium-oxide films are used as a gate insulator in transistors with low leakage currents and threshold voltages [1, 2].

Nominally undoped or doped β-Ga_2O_3 films are used as transparent conductive electrodes, in the development of gas sensors and luminophores and exhibit photoluminescence, cathodoluminescence, and electroluminescence, depending on the fabrication technique and dopant used [3]. The large band gap E_g = 4.6–5.4 eV of gallium oxide makes this material promising for application in optoelectronic devices in the short-wavelength range [4–7].

The electrical and optical characteristics of gallium-oxide films depend on the fabrication technique and subsequent treatment [8–13]. An effective way of controlling the properties of oxide films is by thermal annealing and oxygen-plasma processing [12–14]. Varying the annealing time and temperature, one can intentionally change the optical characteristics of the films. It was demonstrated that, with an increase in the annealing temperature in the range 600–1200°C, the maximum photocurrent at 10 V shifted from 250 to 210 nm [15]. Annealing of the Ga_2O_3 films prepared by rf magnetron sputtering in the range 400–900°C is accompanied by a reduction in sensitivity in the range 230–500 nm [16]. Since the sensitivity decreased most at $\lambda \geq 290$ nm, after annealing at 900°C the ratio between the photocurrent at $\lambda = 230$ nm and the current at $\lambda = 350$ nm was 6×10^3. This means that after annealing ultraviolet (UV) detectors based on Ga_2O_3 films remain solar-blind.

Analysis of the results reported to date shows that it is important to study the optical properties of gallium-oxide films and the photoelectric characteristics of the structures based on them in order to enhance the potential of their application in optoelectronic devices. In this study, we investigate the effect of thermal annealing and processing in oxygen plasma on the photoelectric characteristics of *n*-GaAs–anodic oxide–Ga_2O_3–Me MIS (metal–insulator–semiconductor) structures.

2. EXPERIMENTAL

The Ga_xO_y films were fabricated by the photostimulated (95-W incandescent lamp) electrochemical oxidation of epitaxial GaAs layers (with a donor concentration of $N_d = 8.9 \times 10^{15}$ cm^{-3}) grown in the [100] direction on gallium-arsenide substrates with an electron concentration of $n_0 \approx 10^{18}$ cm^{-3}. The epitaxial-layer thickness was 1.2–2.0 μm. Prior to anodizing, the semiconductor substrates were chemically cleaned to remove the natural oxide and various contaminants.

The cleaning of GaAs involved several operations. A wafer of the semiconductor was boiled in toluene for

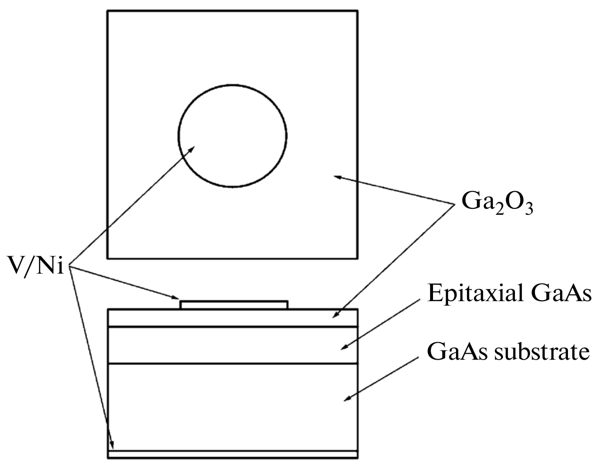

Fig. 1. Schematic representation of the metal–Ga_2O_3–GaAs structure.

10–15 min and in monoethanolamine and dimethylformamide (DMF) mixed in the ratio 1 : 1 for 3 min. The solution was cooled to 45°C, a cassette with the wafer was immersed in a jar with DMF, boiled for 1 min, and cooled in a water bath. To remove DMF from the semiconductor surface, the wafer was washed with deionized water, immersed in a hydrochloric-acid solution HCl : H_2O = 1 : 1 for 3 min, and washed with water again. The final stage was drying in acetone vapors.

Gallium-arsenide films with a thickness of 200–300 nm were grown on the surface of epitaxial GaAs by electrochemical oxidation (anodization). A 0.5% aqueous solution of disubstituted ammonium citrate was used as the electrolyte [12]. Such films can contain arsenic hydride and oxide impurities and foreign atoms and molecules formed during chemical cleaning and anodizing. To remove the reaction co-products, the GaAs wafers with the deposited oxide film were annealed in hydrogen for 10 min at a temperature of 300°C.

After annealing in hydrogen, the gallium-arsenide substrate with the anodic film was divided into several parts. One part was not subjected to annealing and plasma processing; the other parts were annealed at 900°C in argon (open-tube system) for 30 min. Before and after annealing, the gallium-oxide films were exposed to oxygen plasma at a pressure of 3 Pa and a temperature of 50 or 90°C for 0, 10, 20, 30, and 50 min. The gallium-oxide films were treated in a Plasmalab 80 Plus facility (Oxford Instruments). The structure and phase composition of the anodic films before and after oxygen-plasma processing and thermal annealing were determined by X-ray diffraction (XRD) analysis using a Shimadzu XRD-600 diffractometer.

The surface morphology of the films was studied using a Solver HV high-vacuum scanning probe microscope.

To measure the electrical and photoelectric characteristics, 120-nm-thick nickel electrodes with a 30-nm-thick vanadium sublayer were deposited onto the surface of the gallium oxide and rear side of the GaAs (Fig. 1). The area of the upper metal electrode to the Ga_2O_3 film (gate) was 1.04 mm^2. The rear-side contact was continuous.

The effect of radiation on the forward and reverse currents of the structures in the visible range were investigated at wavelengths of 380–700 nm using an incandescent lamp. The average optical power P on the sample was 168 μW. The oxide-film side of the samples was illuminated. To analyze the behavior of MIS structures in the visible range in more detail, we measured the forward and reverse currents under irradiation at a wavelength of 405 nm at several values of the optical power P. The "dark" I–V characteristics and those under illumination were measured using a measuring complex based on a Keithley 2636A dual-channel system sourcemeter and a Nichia NDV4642VFR laser diode.

The spectral dependences of the short-circuit current in the UV range were investigated using an MDR-3 monochromator and a D-2000 Deuterium lamp (Ocean Optics) as a radiation source.

3. RESULTS

According to the XRD data, the as-grown anodic gallium-oxide films are amorphous, have poor adhesion to the substrate, and are easily solved in diluted acidic and alkaline solutions [12, 17].

After exposure to oxygen plasma for 20 min and annealing in argon at 900°C for 30 min, a pronounced peak arises in the XRD spectra, which corresponds to β-Ga_2O_3 crystallites with the [002] orientation, along with the weaker reflections of [311] crystallites and β-Ga_2O_3 crystallites oriented in the [201], [–311], and [600] directions.

Prolonging the oxygen-plasma processing time to 50 min leads to the occurrence of additional peaks in the XRD spectra, which correspond to new crystallites in the Ga_2O_3 film [12]. Similar XRD spectra with a large number of reflections were also obtained when the Ga_2O_3 film was exposed to oxygen plasma after high-temperature annealing.

AFM surface investigations showed that the as-annealed gallium-oxide films have the polycrystalline structure. The average size of crystallites oriented in one direction grows with increasing time of oxygen-plasma processing; the Ga_2O_3-film surface roughness increases several times [12].

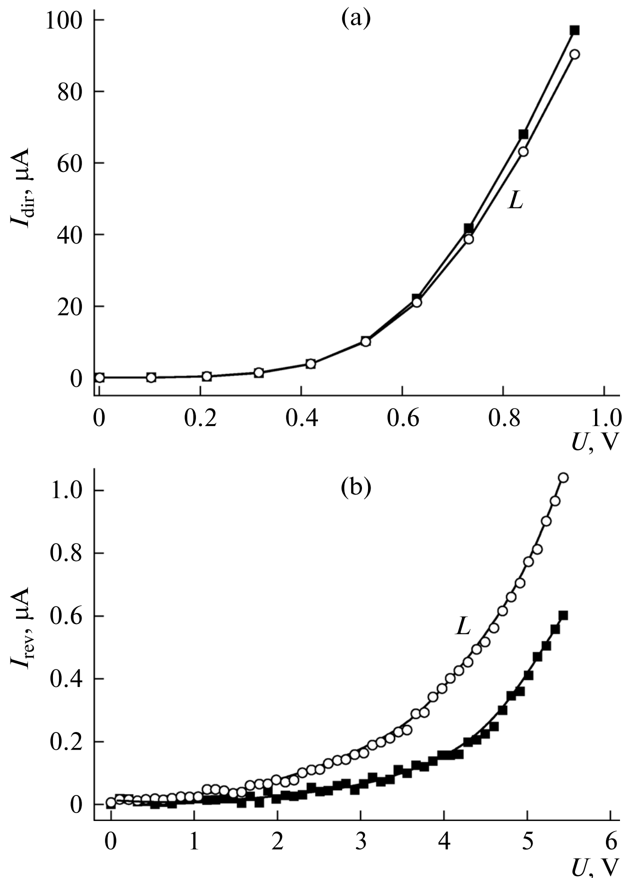

Fig. 2. (a) Forward and (b) reverse *I*–*V* characteristics in darkness and under illumination *L* with visible light.

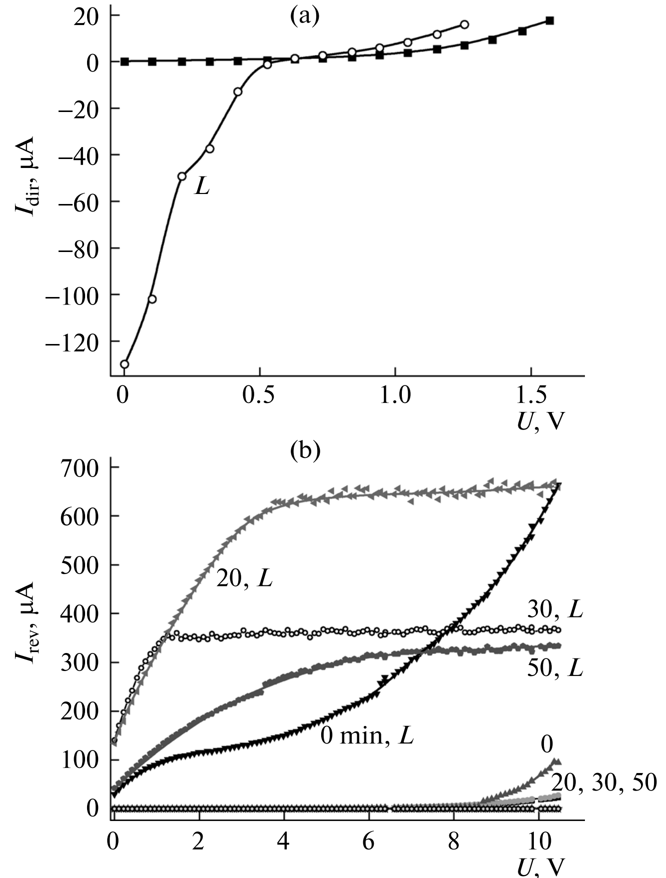

Fig. 3. (a) Voltage dependence of the "dark" current and the current under illumination *L* at positive gate potentials. (b) Voltage dependence of reverse currents in darkness and under illumination *L*. The time of oxygen-plasma processing of Ga_2O_3 is indicated in the figure.

As was shown previously [17], the *I*–*V*, *C*–*V*, and *G*–*V* characteristics of the MIS structures with an unannealed anodic gallium-oxide film depend only slightly on the sign and value of the gate potential. Exposure of the Ga_2O_3 films to oxygen plasma does not significantly change the investigated dependences, but enhances the permittivity of the oxide film. Analysis shows that the investigated samples fabricated using the above-described technique are capacitor-type structures.

Under illumination with visible light, the forward current remains nearly invariable (Fig. 2a) and the reverse current insignificantly increases at the optical power $P = 168$ μW (Fig. 2b).

After annealing at 900°C, the *I*–*V*, *C*–*V*, and *G*–*V* characteristics become asymmetric [18]. Under illumination with incandescent-lamp light of the Ga_2O_3 side, photoresponse is observed only in the samples annealed at a high temperature. Figure 3 shows the "dark" currents and currents under illumination at forward and reverse gate potentials.

The open-circuit voltage increased from 0.34 V for the Ga_2O_3 films without oxygen-plasma processing to 0.84 V upon the plasma-processing time being prolonged to 50 min. The short-circuit current attains its maximum after exposure of the Ga_2O_3 films to oxygen plasma for 20–30 min (Fig. 4).

As the optical power of the radiation at the wavelength $\lambda = 405$ nm is increased, the photocurrent grows, but its values depend on the time of exposure of the oxide film to the oxygen plasma (Fig. 5). At fixed *P*, the photocurrent is larger in the structures exposed to plasma for 20 min (Figs. 5b and 5d). With an increase in the time of oxygen-plasma processing of the Ga_2O_3 film to 50 min, the photocurrent decreases. The obtained data do not contradict the results obtained after illumination by light with wavelengths of 380–700 nm (Fig. 3b).

At positive gate potentials, the currents decrease for the samples that were not exposed to oxygen plasma (Fig. 5a). For the Ga_2O_3 films exposed to oxygen plasma before annealing, the forward currents under

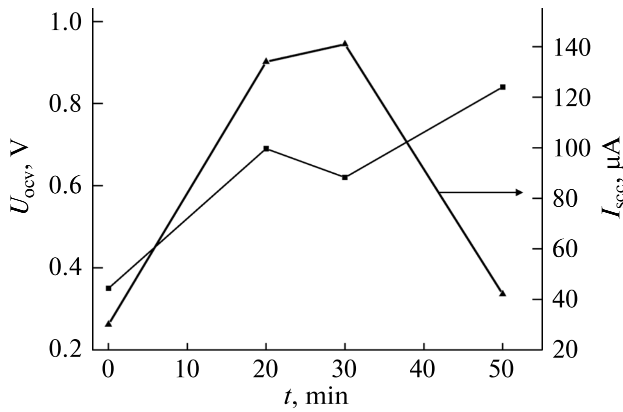

Fig. 4. Dependence of the open-circuit voltage and short-circuit current on the time of oxygen-plasma processing.

illumination grew at almost all P values, starting at a voltage of 0.6 V (Fig. 5c).

The short-circuit current I_{scc} and open-circuit voltage U_{ocv} rapidly increase at low (≤20 μW) P values and tend to saturation as the optical power is further increased (Fig. 6). The data in Fig. 6 correlate with the above-reported results. The power dependence of the photocurrent is determined by the time of sample exposure to oxygen plasma and by the value of the negative gate potential (Fig. 7).

Similar to the behavior of the samples in the visible range, no effect of the UV radiation on the n-GaAs–anodic oxide–Ga_2O_3–Me structures was observed without annealing of the oxide film at 900°C. After annealing, the sensitivity S of the structures in the UV range gradually decreased with a decrease in the wavelength to $\lambda \approx 230–240$ nm and then increases (Fig. 8). The shape of the curves is independent of the oxide-film treatment conditions. The reduction in S in the range 240–400 nm changes to a noticeable increase in the spectral sensitivity with decreasing wavelength. The largest S values at a fixed wavelength are observed for the structures with the gallium-oxide film exposed to oxygen plasma for 20 min before annealing, which corresponds to the behavior of the $I–V$ characteristics in the visible range (Fig. 3b).

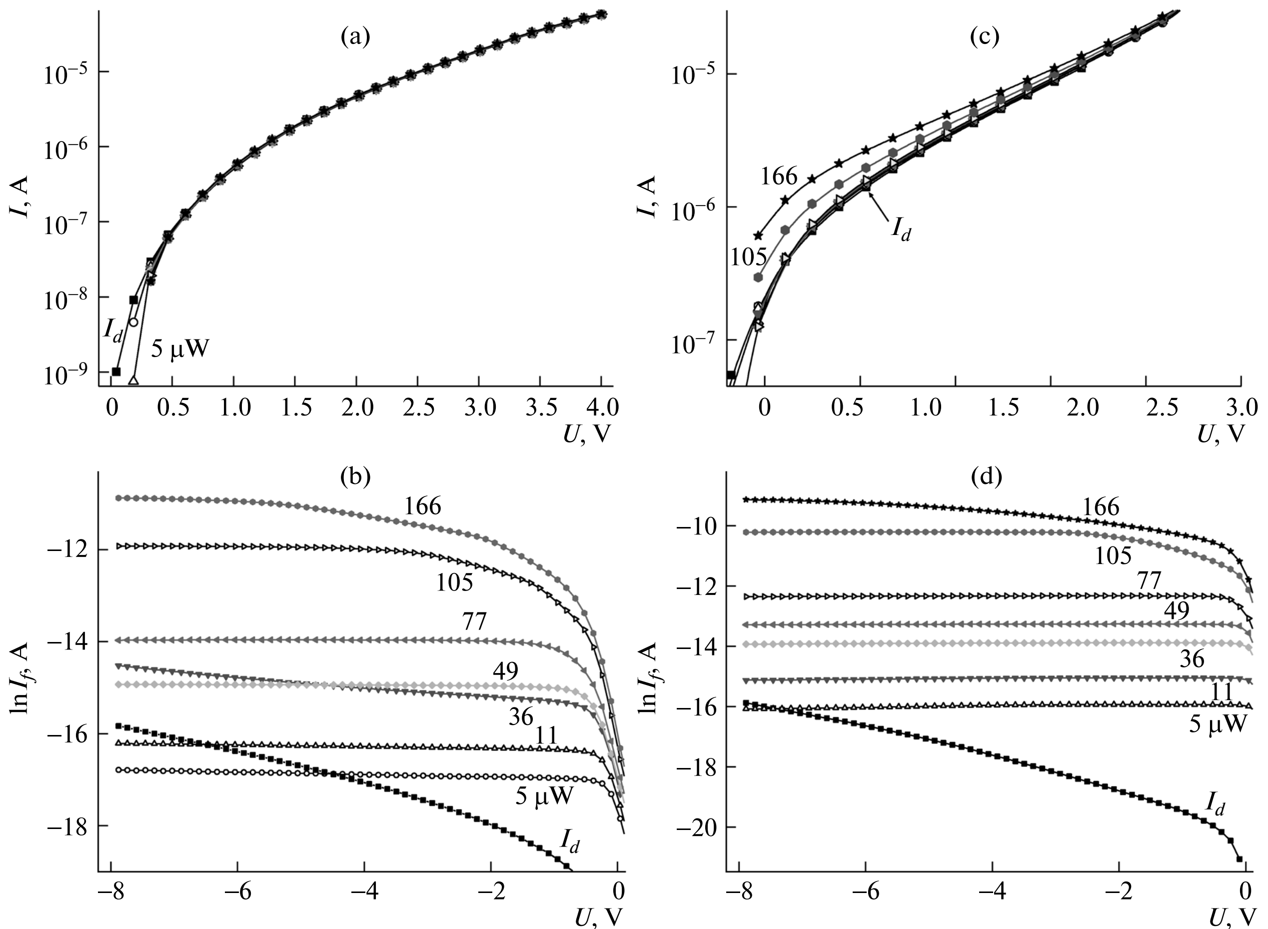

Fig. 5. Currents at (a, c) the positive and (b, d) negative gate potentials (a, b) without and (c, d) with oxygen-plasma processing of the oxide film for 20 min.

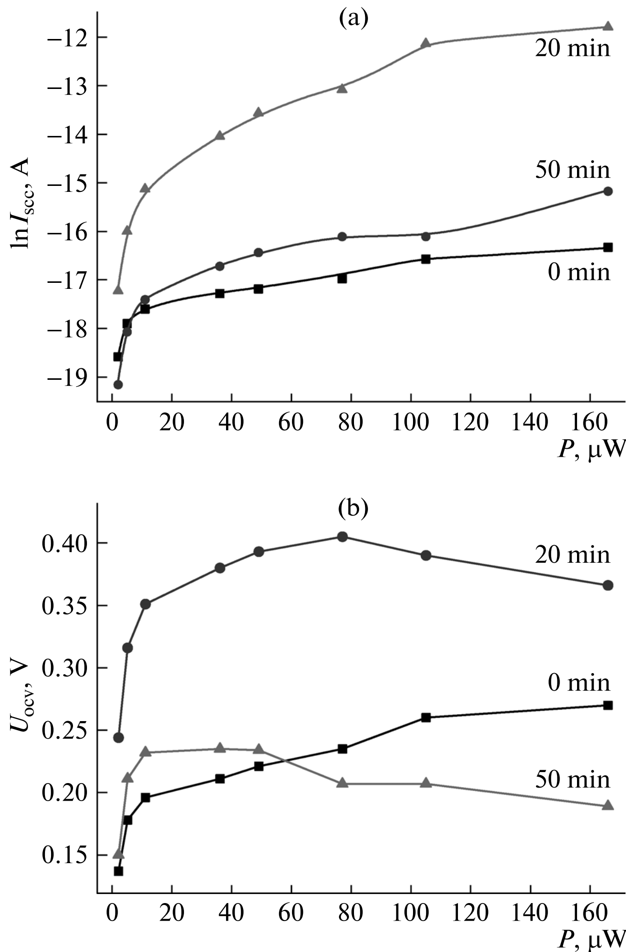

Fig. 6. Optical-power dependences of (a) the short-circuit current and (b) the open-circuit voltage.

4. DISCUSSION

The change in the electrical and optical characteristics of the metal–Ga_2O_3–*n*-GaAs structures after annealing of the gallium-oxide films at 900°C in argon and their exposure to oxygen plasma is caused by the transition of α-Ga_2O_3 to the β phase.

In accordance with the data reported in [5], we suggest that oxygen-plasma processing favors the formation of β-Ga_2O_3 crystallites with different orientations.

Taking into account the Ga_2O_3 and GaAs band gaps, the absence of a photoresponse in the visible range for the unannealed structures is attributed to the nontransparency of the amorphous gallium-oxide film. After annealing in argon, the oxide film becomes polycrystalline β-Ga_2O_3 transparent to visible light. In the range 380–700 nm, the photoresponse of the MIS structures after annealing is caused by the generation of electron-hole pairs both within the space-charge region (SCR) and in the bulk of GaAs at a distance of 2–3 diffusion lengths from the SCR. The ability of the

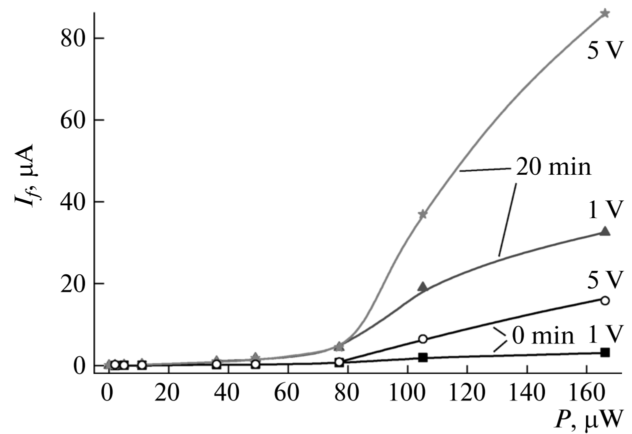

Fig. 7. Optical-power dependences of the photocurrent for the structures exposed to oxygen plasma for 0 and 20 min at negative gate voltages of 1 and 5 V.

Ga_2O_3 films to transmit visible light depends on the time of oxygen-plasma processing. The films exposed to oxygen plasma for 20 min demonstrate the maximum transparency (Fig. 3b).

Analysis of the XRD spectra and AFM images showed that oxygen-plasma processing changes the structure of the anodic gallium-oxide films [12]. As a result, the absorption of light in the Ga_2O_3 film in the visible range is enhanced due to optical transitions with the involvement of defects in the band gap and, as a consequence, the fraction of the optical power absorbed in GaAs decreases.

The highest open-circuit voltages U_{ocv} were obtained for samples with the Ga_2O_3 film exposed to oxygen plasma for 20 min (Fig. 6b). In the most part of the optical-power range, U_{ocv} exceeds almost twice the open-circuit voltages of the structures that were not plasma-processed. The larger U_{ocv} values were obtained for the structures with smaller inverse currents, which corresponds to the formula

$$U_{ocv} = \frac{kT}{e}\ln\left(\frac{I_f}{I_d}+1\right), \quad (1)$$

where I_d is the "dark" current in the structure, k is the Boltzmann constant, T is the absolute temperature, and e is the elementary charge (Fig. 9). In turn, the smaller inverse currents in the Ga_2O_3–GaAs structures exposed to oxygen plasma can be attributed to a decrease in the electron concentration in the epitaxial gallium-arsenide film by one–two orders of magnitude [20].

The forward dark currents at low bias voltages are caused by thermoelectron emission from the semiconductor to the insulator with subsequent transitions to the metal. Under illumination with visible light, electron-hole pairs are generated in gallium arsenide and the countercurrent exceeds the dark current, which

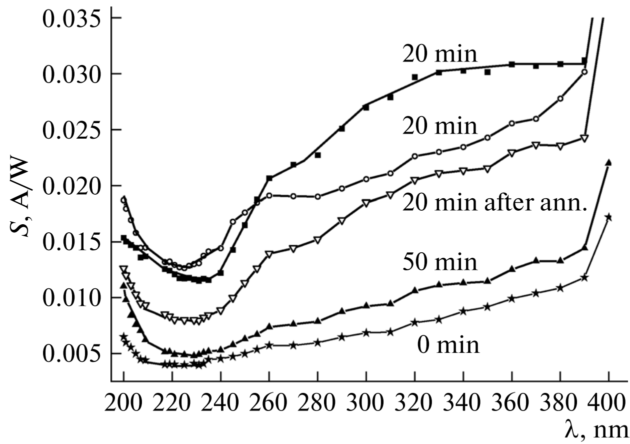

Fig. 8. Spectral sensitivity of the Ga_2O_3–*n*-GaAs structures with a gallium-oxide film annealed at 900°C for 30 min and exposed to oxygen plasma.

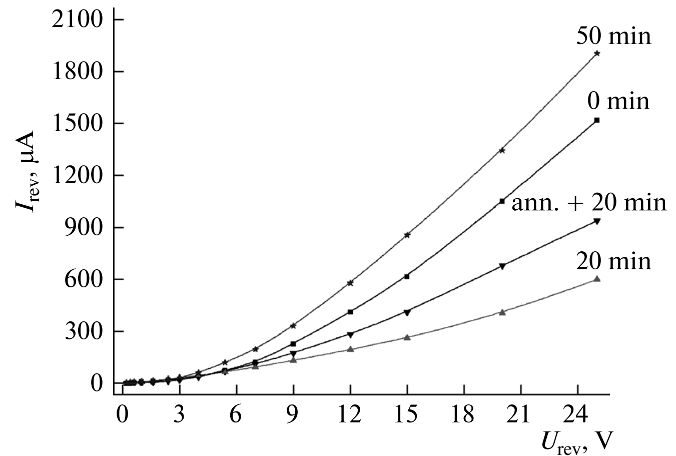

Fig. 9. Reverse *I*–*V* characteristics after exposure to oxygen plasma for 0, 20, and 50 min before annealing and 20 min after annealing.

determines the short-circuit current and open-circuit voltage.

The increase in the forward current under illumination in the structures exposed to oxygen plasma (Fig. 5c) is caused by the photoresistive effect in gallium arsenide due to the presence of a high-resistivity portion near the GaAs–Ga_2O_3 interface. The lower electron concentration in GaAs accounts for the increasing range of positive potentials where the currents change under illumination in the structures exposed to oxygen plasma for 20 min.

In the short-wavelength portion of the visible range, the spectral sensitivity of gallium arsenide decreases and the transmittance of the Ga_2O_3 films decreases [8–10]. As a result, the sensitivity of the GaAs–Ga_2O_3 structures decreases and takes its minimum value at $\lambda = 230$–240 nm. Taking into account the known Ga_2O_3 band-gap values, we may assume that the increase in S at $\lambda < 240$ nm is related to an increase in the current due to absorption in the gallium-oxide film. The enhancement of absorption with a decrease in the wavelength was observed in [14] for the gallium-oxide films deposited by pyrolysis on quartz and sapphire substrates.

The reduction in the sensitivity S with an increase in the time of oxygen-plasma processing to 50 min is probably caused by the occurrence of defects both at the GaAs–Ga_2O_3 interface and in the bulk of the oxide film. Another cause for the S reduction can be an increase in the oxide-film thickness due to the interaction between oxygen atoms and semiconductor components.

4. CONCLUSIONS

The effect of thermal annealing in argon at 900°C for 30 min and oxygen-plasma processing on the photoelectric characteristics of GaAs–Ga_2O_3–metal structures with a gallium-oxide film prepared by electrochemical oxidation was investigated under illumination in the visible and UV ranges. The results obtained allow us to draw the following conclusions:

(i) Unannealed anodic gallium-oxide films are not transparent to visible and UV radiation, which accounts for the absence of the photocurrent in the investigated structures.

(ii) Annealing at 900°C sharply increases the transparency of the films and gives rise to photocurrent in the MIS structures.

(iii) The change in the forward and reverse *I*–*V* characteristics in the visible range is determined by the absorption of light in GaAs.

(iv) The photocurrent and its voltage dependence are determined by the time of oxygen-plasma processing, which is due to the variation in the phase composition of the oxide film and the appearance of defects in gallium arsenide.

(v) The sensitivity in the UV range decreases to 230 nm and increases with a further decrease in the wavelength, which is attributed to predominant radiation absorption in the gallium-oxide film.

ACKNOWLEDGMENTS

This study was supported by the Ministry of Education and Science of the Russian Federation, project no. 1206.

REFERENCES

1. R. Droopad, M. Passlack, N. England, K. Rajagopalan, J. Abrokwah, and A. Kummel, Microelectron. Eng. **80**, 138 (2005).
2. O. Seok, W. Ahn, Y.-S. Kim, M.-W. Ha, and M.-K. Han, http://www.intechopen. com/books/semiconductortechnologies/gan-based-metal-oxide-semiconductor-devices

3. S. K. Gupra, J. Sinh, and J. Akhtar, http://www.intechopen.com/books/physics-and-technologyof-silicon-carbide-devices/materials-and-processing-for-gate-dielectrics-on-silicon-carbide-sic-surface
4. S. Nakagomi, T. Moto, S. Takahashi, and Y. Kokubun, Appl. Phys. Lett. **103**, 072105 (2013).
5. T. Oshima, T. Okuno, N. Arai, N. Suzuki, S. Ohira, and S. Fujita, Appl. Phys. Express **1**, 011202 (2008).
6. R. Suzuki, S. Nakagomi, Y. Kokubun, N. Arai, and S. Ohira, Appl. Phys. Lett. **94**, 222102 (2009).
7. Y. Kokubun, K. Miura, F. Endo, and S. Nakagomi, Appl. Phys. Lett. **90**, 031912 (2007).
8. F. K. Shan, G. X. Liu, G. H. Lee, I. S. Kim, and B. C. Shin, J. Appl. Phys. **98**, 023504 (2005).
9. Y. Zhang, J. Yan, Q. Li, C. Qu, L. Zhang, and T. Li, Physica B **406**, 3079 (2011).
10. L. Kong, J. Ma, C. Luan, W. Mi, and Y. Lv, Thin Solid Films **520**, 4270 (2012).
11. S.-A. Lee, J.-Y. Hwang, J.-P. Kim, S.-Y. Jeon, and C.-R. Cho, Appl. Phys. Lett. **89**, 182906 (2006).
12. V. M. Kalygina, A. N. Zarubin, E. P. Naiden, V. A. Novikov, Yu. S. Petrova, O. P. Tolbanov, A. V. Tyazhev, and T. M. Yaskevich, Semiconductors **46**, 267 (2012).
13. V. M. Kalygina, A. N. Zarubin, V. A. Novikov, Yu. S. Petrova, O. P. Tolbanov, A. V. Tyazhev, S. Yu. Tsupii, and T. M. Yaskevich, Semiconductors **47**, 612 (2013).
14. T. M. Yaskevich, D. L. Budnitskii, V. M. Kalygina, N. I. Kozhinova, I. A. Prudaev, and I. M. Egorova, Izv. Vyssh. Uchebn. Zaved., Ser. Fiz. **56** (8/3), 153 (2013).
15. Y. Kokubun, K. Miura, F. Endo, and S. Nakagomi, Appl. Phys. Lett. **90**, 031912 (2007).
16. S.-T. Su, W. Y. Weng, C. J. Chiu, and S. J. Chang, National Cheng Kung University. http://ir.lib.ncku.edu.tw/retrieve/104641/Effect+of+Thermal+Annealing+on+Ga_2O_3-Based+Solar-Blind+Photodetectors+Prepared+by+RF+Sputter_Abstract.pdf
17. V. M. Kalygina, A. N. Zarubin, E. P. Naiden, V. A. Novikov, Yu. S. Petrova, M. S. Skakunov, O. P. Tolbanov, A. V. Tyazhev, and T. M. Yaskevich, Semiconductors **45**, 1097 (2011).
18. V. M. Kalygina, K. I. Valiev, A. N. Zarubin, Yu. S. Petrova, O. P. Tolbanov, A. V. Tyazhev, and T. M. Yaskevich, Semiconductors **46**, 1003 (2012).
19. J. Hao and M. Cocivera, J. Appl. Phys. D: Appl. Phys. **35**, 433 (2002).
20. V. M. Kalygina, V. V. Vishnikina, A. N. Zarubin, Yu. S. Petrova, M. S. Skakunov, O. P. Tolbanov, A. V. Tyazhev, and T. M. Yaskevich, Russ. Phys. J. **56**, 984 (2014).

Translated by E. Bondareva