Electrical and photoelectric characteristics of gallium oxide films obtained by RF magnetron sputtering

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Abstract. In order to investigate dependence of conductivity on the temperature and photoresponse of $\beta$-Ga$_2$O$_3$ thin films, films were grown by a radio frequency magnetron sputtering on sapphire substrates. The conductivity of films without annealing depends weakly on the temperature to 560 °C and increase exponentially at $T > 560$ °C. After annealing at 900 °C growth region shifts to 350 °C. Films without annealing are solar-blind and have a photoresponse to illumination with a wavelength of 222 nm.

1. Introduction.
At present, attention is focused on gallium oxide. There are five phases in which Ga$_2$O$_3$ can exist: $\alpha$, $\beta$, $\gamma$, $\delta$, $\varepsilon$-phases [1]. Of all five phases, two are distinguished: $\alpha$- and $\beta$-phases. They are the most stable. The oxide has a transparency of about 90% over the entire visible range, to the ultraviolet region and wide bandgap about $4.9 \text{eV}$ [2]. The conductivity of gallium oxide depends on many factors: the method of preparation, the temperature of the substrate, the partial pressure of oxygen in the chamber, the ambient temperature, the doping, the chemical composition of the substrate, the further treatment of Ga$_2$O$_3$, etc. Wide band gap materials offer the possibility of fabricating high power density electronic devices, deep-ultraviolet transparent electrode, short wavelength optical emitter and deep-ultraviolet transparent photodetector [3].

2. Experiment details.
This report discusses the results of investigations of gallium oxide films obtained by radio frequency magnetron sputtering. Films 150-200 nm in thickness were deposited by magnetron sputtering of a Ga$_2$O$_3$ target (99.9999%) onto non-heated sapphire substrates in an AUTO-500 unit (manufactured by Edwards) in an Ar / O$_2$ gas mixture. The oxygen concentration in the mixture was maintained at $(56.1 \pm 0.5)$ vol.%. The distance between the target and the substrate was 70 mm. The pressure in the chamber during the deposition was $7 \cdot 10^{-3}$ mbar.

After deposition of gallium oxide, the substrate with the film was divided into two parts. One part was left without treatment. The second part was annealed in argon for 30 minutes at a temperature of 900 °C. The structure and phase composition of the gallium oxide films were determined by X-ray diffraction analysis (RDA) using a Lab-X XRD 6000 Shimadzu X-ray diffractometer. Analysis of the surface of the sputtered films was carried out using an atomic force microscope "Solver HV".
The conductivity was recorded in a special chamber. Samples were placed in holders and placed in a chamber whose relative humidity was maintained at 32%. The temperature was increased from 50°C to 590°C.

Photoelectric characteristics were taken using Keithley 2611. At first measurements were carried out without applying radiation to the samples, then the samples were isolated from the light and subsequently irradiated at a wavelength of 400 nm and 222 nm using a light-emitting diode and a special ultraviolet lamp, respectively.

3. Results and discussion.

According to X-ray diffraction analysis, films obtained under the conditions described above and not subjected to annealing at high temperature turn out to be polycrystalline, contain crystallites of α- and β-phases of gallium oxide (Fig. 1a). The α-phase disappears after annealing in argon at 900 °C for 30 minutes, and the β-phase crystallites remain with different crystallographic planes (Fig. 1b).

![Figure 1](image)

Figure 1. Spectra of X-ray diffraction of Ga₂O₃ films before annealing in Ar (a) and after 30 minutes of annealing in argon at a temperature of 900 °C (b).

The polycrystalline structure of gallium oxide films not subjected to any treatment is confirmed by AFM data (Fig. 2). The average size of the crystallites is 40 nm (Fig. 2c).
Figure 2. The surface of the oxide film not subjected to high-temperature annealing: a) – image of the surface of the film; b) – the volumetric dimensions of the film; c) – the crystallite size.

The oxide film after annealing in argon at 900 contains crystallites whose average size is 90 – 100 nm (Fig. 3).
Figure 3. The surface of the oxide film after annealing at 900 °C: a) – image of the surface of the film; b) – the volumetric dimensions of the film; c) – the crystallite size.

Measurements of electrical and photoelectric characteristics were carried out on samples of a planar design. Films obtained on sapphire substrates and not subjected to thermal annealing had resistances of the order of $10^9 - 10^{10}$ Ωm. In the interval 50 – 500 °C, the conductivity of the samples ($G$) depends weakly on the temperature $T$ and increases exponentially with a further increase in temperature (Fig. 4a). The activation energy of conduction growth in the high-temperature region is 0.7 – 1.0 eV.

After annealing the gallium oxide films in argon for 30 minutes at 900 °C, the region of sharp increase in conductivity at the temperature dependence of $G$ ($1/T$) shifts to lower temperatures and begins at $T \approx 350$ °C (Fig. 4b). The activation energy of the increase in $G$ with increasing temperature for most of the samples is 0.3 – 0.5 eV. The curve of the dependence of $G$ on $1/T$ shows a maximum in the range 470-520 °C.

Figure 4. Temperature dependence of the conductivity of gallium oxide films on Al₂O₃ without (a) and after annealing (b) at 900 °C; on the inset: the temperature dependence of the conductivity in the coordinates ln($G$) from $1/T^{1/4}$.
In the course it was found that samples without annealing are solar-blind and have no photoresponse on wavelength 222 nm (Fig. 5a).

Ga₂O₃ remains solar-blind after annealing. Lighting with $\lambda = 400$ nm does not lead to a change in the VAC, whereas radiation with $\lambda = 222$ nm causes a noticeable increase in current, which depends on the voltage on the sample (Fig. 5b). The absence of a photoresponse when exposed to light with $\lambda = 400$ nm is most likely due to the fact that the energy quantum of this radiation is $h\nu = 3.1$ eV less than the width of band gap of gallium oxide $E_g = 4.8 – 4.9$ eV.

![Figure 5](image)

Figure 5. The volt-ampere characteristics of gallium oxide before annealing in Ar and after annealing; without (a) and during exposure to radiation (b). The wavelength is shown in the figure; the dark current is denoted by the letter D.

4. Conclusions

Annealing at 900 °C causes a change in the surface of the film: the size of the crystallites increases twofold in comparison with the film without annealing.

The structures obtained on a dielectric substrate turn out to be solar-blind in the visible wavelength range and are sensitive to the effects of radiation in the UV-range.

After annealing Ga₂O₃ in Ar at 900 °C growth region of conductivity shifts to 350 °C.

References

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