Non-equilibrium methods for synthesis and modification of gallium oxide

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Abstract. Synthesis and modification of gallium oxide as a wide-bandgap semiconductor is a topical task in the fields of power electronics, UV detectors, gas sensors, telecommunication. In the present work, the Ga₂O₃ films deposited on sapphire substrates by magnetron sputtering have been studied. The influence of deposition parameters and subsequent annealing on the structure and optical properties of the synthesized films is analyzed. Ion doping of magnetron-deposited films with silicon is carried out by the ion implantation method. It is shown by the Raman scattering and optical transmission spectroscopy that ion irradiation leads to the disordering of the crystal structure, but subsequent annealing results in a partial recovery of the structure. Hall-effect measurements for irradiated and then annealed films do not reveal the formation of a conducting layer. Apparently, this is due to the fact that the main contribution to the resistance is made by grain boundaries in the magnetron-deposited films.

1. Introduction
For more than half a century, silicon has been (and still is) the main semiconductor material in electronic engineering. However, in the number of technologies, such as power electronics and sensorsics, the demand for wide-bandgap semiconductors has increased. The leading positions among such semiconductors in a number of important and unique properties are taken by gallium oxide and, especially, its most stable β-modification with bandgap of 4.5-4.9 eV [1-6]. Due to its wide bandgap, gallium oxide can be used to create high-temperature gas sensors, solar-blind UV detectors, power diodes and transistors, thin-film electroluminescent displays, etc. [1,4,7-9]. Gallium oxide samples are sufficiently resistant to radiation and can retain their properties at high temperatures and in aggressive environments [7]. Bulk crystals of large diameter can be grown and are used as substrates in epitaxy [10].

As it is well known, microelectronics owes its unprecedented success to ion implantation, which is a key method in the technology of practically all semiconductor devices [11]. Among the advantages of this method are the precise dosage of dopants; the ability to control their space distribution and the use of radiation defects generated by ion irradiation ("defect engineering"); relatively low temperatures required in technology. The importance of ion implantation for Ga₂O₃ further increases...
due to the difficulty of obtaining a p-type material [1,12]. To overcome this problem, the use of such a "non-equilibrium" method as ion implantation seems to be promising.

Investigations in the field of ion implantation in Ga$_2$O$_3$ began quite recently and have so far raised only a relatively small range of fundamental and applied problems [6]. Nevertheless, the promising nature of this method has already been demonstrated for a number of important practical applications. In particular, the possibility of a significant improvement in the properties of ohmic contacts and the formation of field-effect transistors channels by ion doping are established, the possibility of a controlled increase in the resistivity of n-Ga$_2$O$_3$ by ion doping with acceptor impurities is found, and a method of ion synthesis and ion modification of nanostructures is developed to create optoelectronic devices [6]. In addition to the ion implantation method, there is a method of magnetron sputtering in which ion irradiation occurs during the film growth [13]. Deviation from equilibrium conditions is also possible in its implementation, which makes it possible to use defect engineering, as in the case of ion implantation.

The most common donor impurities in Ga$_2$O$_3$ technology are Si, Ge, and Sn [5,6]. There are some attempts to achieve p-type conductivity, for example, using Mg or Zn doping [14,15], but these impurities form only deep acceptor levels and cannot lead to p-type conductivity [15,16].

In the present work, the results of studying the effect of magnetron deposition parameters on the properties of Ga$_2$O$_3$ films deposited on sapphire substrates, as well as the modification of structural, optical, and electrical properties of magnetron-deposited Ga$_2$O$_3$ films by ion implantation followed by annealing are demonstrated.

2. Experimental

The deposition of Ga$_2$O$_3$ films on c-sapphire (0001) substrates was carried out using an upgraded UVN-2M vacuum system. During the growth process, the radio frequency (RF) generator power, the pressure in the working chamber, and the parameters of subsequent annealing were varied. Si implantation was carried out for the Ga$_2$O$_3$ magnetron-deposited films obtained at Tomsk State University using a commercial Edwards Auto-500 system. After implantation, the samples were annealed in a dried nitrogen atmosphere (30 min). The samples characterization was carried out by Raman scattering and optical transmission spectroscopy, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) methods, and by measuring the Hall effect (with indium contacts).

3. Results and discussion

For the Ga$_2$O$_3$ films deposited on sapphire without heating the substrate (deposition time 20 min) and sequentially annealed at 750 °C and 900 °C for 30 min, the changes in the working gas pressure and RF power significantly affect the parameters of spectral lines in the Raman spectra (Figure 1). In this case, the best result in terms of structural quality is achieved at relatively low pressures and high annealing temperatures. According to the Raman data, gallium oxide is formed in the β-phase.

![Figure 1](image-url)  
**Figure 1.** Dependence of Raman spectra on annealing temperature of Ga$_2$O$_3$ magnetron films (a), working pressure, and RF power during the deposition of these films (b).
To study the effect of Si\textsuperscript{+} implantation on the properties of gallium oxide films, the properties of the as-deposited films were first determined. Directly after deposition, the film has an amorphous structure according to XRD data; in the XRD diffraction pattern, no any Ga\textsubscript{2}O\textsubscript{3} reflection peaks were observed. After annealing at 900 °C (30 min) in an argon atmosphere, the film transforms into a polycrystalline state. XRD diffraction pattern contains reflection peaks which are attributed to the (-201), (-402), (-603), (-204) and (512) reflections of the β-Ga\textsubscript{2}O\textsubscript{3} [17]. According to the AFM data with the formation of step by photolithography, the film thickness is 138 nm. Si\textsuperscript{+} irradiation was carried out with an energy of 85 keV and doses of 2\times10\textsuperscript{14}, 4\times10\textsuperscript{14} and 8\times10\textsuperscript{14} cm\textsuperscript{-2}. According to the SRIM calculation [18], the average projected range is \(R_p = 67\) nm and the straggling is \(\Delta R_p = 29\) nm. The selected irradiation conditions provide the distribution of implanted atoms within the film thickness.

According to the Raman data (Figure 2), irradiation of polycrystalline films leads to disordering the crystal structure. With subsequent high-temperature annealing, the Raman lines become more intense, and at the same time, a tendency to a decrease in the linewidth is observed. Both of these facts indicate a partial recovery of the structural quality of the film upon annealing. Moreover, the larger the dose is, the lower is the degree of recovery at a given temperature.

Figure 2. Raman spectra for magnetron-deposited Ga\textsubscript{2}O\textsubscript{3} films on sapphire irradiated with silicon ions and subsequently annealed. FA means “furnace annealing”. For clarity, the data only for one ion dose are shown.

To determine the effective bandgap, the optical transmission spectra and XPS data were analysed. The results demonstrate that ion irradiation leads to a decrease in the effective band gap \(E_g\) depending on the ion dose. Subsequent annealing at 700 °C leads to the reduction of \(E_g\), but, upon additional annealing at 950 °C, the \(E_g\) values become even higher than the initial ones. The values of the bandgap for the films vary from 4.6 eV to 4.9 eV according to optical transmission data plotted in the \((\alpha h\nu)^{-1}\) vs. \(h\nu\) coordinates (Figure 3), where \(h\) is Planck’s constant, \(\nu\) is the frequency of light, \(\alpha\) is the absorption coefficient.
Figure 3. Dependence of $(a\nu)^2$ on $\nu$ for magnetron-deposited $\text{Ga}_2\text{O}_3$ films on sapphire irradiated with silicon ions and subsequently annealed.

In order to establish the effect of Si ion doping on the electrical properties of these films under the same conditions of implantation and annealing, experiments with bulk semi-insulating $\beta$-$\text{Ga}_2\text{O}_3$ samples (010) were also carried out. The use of semi-insulating samples eliminates the shunting of the conductivity by the volume of the wafer. The results of the Hall-effect measurements show that a low-resistance $n$-type layer (resistivity of $139$ $\Omega$·cm) is formed in bulk samples upon ion doping (this agrees with the literature data [19]) with concentration of the main charge carrier of $2.4\times10^{14}$ $\text{cm}^{-3}$, and mobility of $9.5$ $\text{cm}^2/V\cdot\text{s}$. For the polycrystalline magnetron films under the indicated conditions, it is not possible to detect the presence of a conducting layer under the conditions used in the work. Apparently, this is due to the fact that the main contribution to the resistance is made by grain boundaries in such films. The transition to electrically active state of Si atoms implanted into the grain boundaries is difficult due to the interaction with grain-boundary defects and due to the amorphous-like state of the material within the boundaries, at least under our experimental conditions.

The assumption about the role of the gallium oxide grain boundary is supported by the optical transmission spectroscopy data, which show that the effective bandgap after annealing became larger than in that of the initial gallium oxide films. This may be due to the Burstein-Moss effect – the filling of the lower levels of the conduction band with electrons in the gallium oxide grains ion-doped with silicon. In this case, the film resistance is completely determined by the grain boundaries, remaining in a high-resistivity state.

4. Conclusions
The properties of $\beta$-$\text{Ga}_2\text{O}_3$ films deposited by magnetron sputtering on sapphire substrate and subjected to ion implantation have been studied. It is assumed that the use of non-equilibrium methods of synthesis and modification of properties will contribute to solving such an important problem as obtaining $p$-type gallium oxide, which is prevented by the peculiarities of its energy structure under equilibrium conditions.

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