Plasma-chemical deposition of gallium oxide layers by oxidation of gallium in the hydrogen-oxygen mixture

L A Mochalov¹,²,³, A A Logunov¹* and M A Kudryashov¹

¹ Department of Nanotechnology and Biotechnology, Nizhny Novgorod State Technical University n.a. R.E. Alekseev, Nizhny Novgorod, 24 Minina street, 606950 Russia
² Department of Physics and optical science, University of North Carolina at Charlotte, Charlotte, 9201 University City Blvd, NC 28223-0001, USA
³ Sirius University of Science and Technology, Sochi, 1 Olympic Ave, 354340 Russia

* alchemlog@gmail.com

Abstract. Gallium oxide is an ultra wide band gap (the width of the band gap is 4.85 eV) transparent semiconducting oxide, that nowadays attracts much attention of scientists and manufacturers. However, the main obstacle, preventing from its massive commercial implementation, is the lack of technological methods to its production; it is supposed to be cheap, reproducible, and scalable. In this work we are developing a novel plasma-chemical method of Ga₂O₃ thin films’ synthesis; according to this method only high-purity elemental gallium was used as the source of gallium delivered by the hydrogen flow into the plasma discharge zone, where the interaction with oxygen took place. The properties of the solid phase obtained in the conditions of heteroepitaxial growth were studied depending on the experimental parameters.

1. Introduction
Gallium oxide is attractive for the use in the UV applications, as it is a wide-gap semiconductor (4.6-4.9 eV) with a sufficient conductivity to create vertical devices on its basis; these devices can provide the highest energy efficiency. As a conductive transparent material Ga₂O₃ can solve not only the problem of a conductive substrate, but also replace other oxides in the design of the LED chips. However, the device’s main characteristics such as sensitivity, performance, durability etc. are determined by the structural quality and properties of the gallium oxide epitaxial layer. Gallium oxide thin films may be prepared by different techniques [1-5]. Heteroepitaxial β-Ga₂O₃ films, usually of a poor structural quality (FWHM> 1000 arc sec), can be obtained both amorphous or polycrystalline. Homoeptaxial β-Ga₂O₃ layers can be applied by MOVPE/MOCVD method on the orienting β-Ga₂O₃ substrates made from the bulk crystals [6-12]. Although very promising results were achieved on (010) substrates, their preparation is really expensive and complicated as they must be sliced perpendicularly to both easy cleavage planes. The general problem of the existing deposition techniques is also in usage of the volatile derivatives of gallium, e.g., MOC or gallium chlorides, as the source of gallium; this is the reason for appearance of additional contamination of the gallium oxide layer with the products of the precursors’ incomplete conversion.
The main objective of this work is to elaborate a new method of heteroepitaxial β-Ga2O3 growth on the c-sapphire substrates.

2. Experimental part
The experiments were carried out on the plasma-chemical installation described in detail in [13-16]. The installation included a gas supply system, a plasma-chemical tubular reactor made of high-purity quartz glass with the inner diameter 25 mm, and a pumping system. The gas supply system consisted of pressure reducers, mass flow controllers and a vacuum flange interconnected by stainless steel tubes. The vacuum flange connected the gas supply system with the plasma-chemical reactor, and it also served for the loading of the source high-purity gallium. The part of the reactor with the loaded gallium was equipped with the external heater, and the other part was equipped with the outer inductor to ignite the plasma discharge. A RF generator with the 40 MHz frequency with a matching unit was used. The generator’s power was varied in the range of 20-70 W. The substrates were placed perpendicular to the flow by a special holder directly into the discharge zone. High-purity hydrogen was used as a carrier gas being blown with a constant rate through the reservoir with gallium. High-purity oxygen was delivered directly into the plasma discharge zone. The total flow rate was 30 ml/min at the general pressure in the system - 1×10⁻¹ Torr. The temperature of the gallium source was 750 °C; c-sapphire with size 10×10 mm was used as the substrates.

3. Results and discussion
3.1. Optical emission spectroscopy (OES) of Ga-H2-O2 mixture’s plasma at different ratios of oxygen and hydrogen
First of all, the influence of the (oxygen/hydrogen) ratio in the initial gas phase on the mechanism of the plasma-chemical process was studied [17-19]. The optical emission spectra of the Ga-H2-O2 mixture’s plasma at various ratios of hydrogen and oxygen, measured in the range of 250-550 nm, are shown in Figure 1. In this case, the total flow rate remained constant 30 ml/min, the total pressure in the system was 0.1 Torr, the temperature of the gallium source was 750 °C, and the generator’s power was constantly 50 W. While carrying out the experiments, the gas ratios of O2/H2 were 2/1, 1/1 and 1/2 (the ratios are given in moles). For comparison the spectrum of the binary mixture (Ga-H2) is shown in Figure 1a. In the absence of oxygen, the plasma spectrum contains emission lines of gallium atoms Ga (I) at 287.4, 294.4, 403.3, 417.2 nm and molecular and atomic emission lines of hydrogen in the range of 460 - 950 nm.

An addition of oxygen to the Ga-H2 mixture up to the ratio 2/1 (Figure 1b) is accompanied by a significant decrease in the intensity of the Ga (I) and H2 (I) lines. In addition, the intensity of the atomic lines of hydrogen H (I) at 486.1, 656.3 nm slightly increases and weak lines from oxygen-containing fragments O (I), O (II), OH (I) appear in the areas of 450 - 500 nm and 680 - 950 nm. The band at 634 nm is attributed to the emission of a dimer of two excited oxygen molecules O2(^1Δ), which are simultaneously deactivated with the emission of one quantum:

\[ O_2(^1Δ) \rightarrow O_2(^3Σ) + hν(634nm), \]  

In [20] it was shown that the 634 nm line is convenient for monitoring the concentration of singlet O2(^1Δ), as its intensity is proportional to the square of the O2(^1Δ) concentration. It was found out by EPR and mass spectrometry [21] that the concentration of singlet oxygen in the RF plasma is about 10% of the total oxygen concentration in the flow. In addition to singlet oxygen, the authors [22-24] showed the formation of ozone and atomic oxygen in a gas discharge. Low-intensity lines in the range of 417-425 nm, based on the data of quantum-chemical modelling, were attributed to the excited fragments [Ga3O]/*. The further increase of oxygen in the mixture to the ratios 1/1 (Figure 1c) and 1/2 (Figure 1d) does not change practically the intensity of the Ga (I) emission lines. In the area up to 300 nm, gallium lines are not observed due to the strong absorption of radiation by the excess of oxygen in this area. As it will be shown below, among the ratios chosen the H2:O2 = 2:1 turned out to be optimal.
in terms of surface quality of Ga$_2$O$_3$ films. The increase of oxygen above this ratio leads to the increase of the average crystallite size and to the growth of the polycrystalline β-Ga$_2$O$_3$ phase. However, the epitaxial layers are still considered to be the most interesting from the point of view of creating the future devices. The increase in the hydrogen ratio, in turn, leads to the increase of the rate of the hydrogen etching of the deposited films; this has a positive effect on the degree of the layers’ crystallinity, but significantly reduces the velocity of their growth.

![Emissive spectra of the mixtures: a – Ga+H$_2$; b – Ga+H$_2$O$_2$ (2:1); c – Ga+H$_2$O$_2$ (1:1); d – Ga+H$_2$O (1:2). In the insertion – the entire spectra are in the range of 200 – 1100 nm.](image)

**Figure 1.** Emissive spectra of the mixtures: a – Ga+H$_2$; b – Ga+H$_2$O$_2$ (2:1); c – Ga+H$_2$O$_2$ (1:1); d – Ga+H$_2$O (1:2). In the insertion – the entire spectra are in the range of 200 – 1100 nm.

3.2. Dependence of the surface morphology of the gallium oxide films on the power in the plasma discharge

The dependence of the surface morphology of the gallium oxide films on the power in the plasma discharge on the sapphire substrate according to AFM data is shown in Figure 2. The increase of the plasma power up to 30 W leads to a more noticeable growth of the pyramidal crystalline structural fragments in the amorphous matrix. According to scientific literature data [25, 26], pyramidal fragments are likely to represent the ε-Ga$_2$O$_3$ phase, or, as it is stated in some scientific literature sources, β-Ga$_2$O$_3$ with a large number of dangling bonds and structural defects. According to the AFM data, the average size of such pyramidal crystallites is $500 \times 10^2$ nm$^2$ (the variation coefficient is 28 %) with the surface roughness – $R_a = 5.85$ nm and $R_z = 30.25$ nm. The further increase of the plasma discharge power results in the formation of the uniform polycrystalline material consisting of cubic crystallites with the average size of $470 \times 10^2$ nm$^2$ with a narrow distribution (the variation coefficient is only 11 %), with the structure surface roughness $R_a = 4.40$ nm, $R_z = 21.30$ nm. At the minimum plasma power 20 W, the thin film was deposited as a predominant amorphous phase with inclusions in the form of islands consisting of pyramidal structural fragments. The average surface roughness of such a film was $R_a = 1.58$ nm, $R_z = 19.30$ nm, while the average crystallite size in island fragments was $615 \times 10^2$ nm$^2$. 
As it can be concluded from the data obtained, the increase in the power applied in the plasma discharge led to the sharp change in the phase composition of the films’ roughness; cubic crystallites, according to the scientific literature data, represent the β-phase of Ga₂O₃, the formation of which was considered possible only at the substrate temperatures above 600-650 °C or during the following thermal annealing in the oxygen atmosphere [25].

Thus, it has been shown that, in the conditions of our experiments, the direct formation of the polycrystalline β-phase of gallium oxide on the substrate becomes possible. At the maximum power of the plasma discharge in the conditions of our experiments, the epitaxial β-Ga₂O₃ layer is formed. In
this case the resolution of the electron microscope turned out to be insufficient to study such thin layers; this is typical of epitaxial structures. Consequently, the proposed synthesis method, as it was expected, allows us to obtain β-Ga₂O₃ epitaxial layers required for various devices and applications.

3.3. The influence of the substrate temperature on the surface morphology of the gallium oxide films
Since in the conditions of our experiments the c-sapphire substrate offers a maximum structural diversity of the obtained materials; on the example of this material the influence of the substrate temperature on the morphology of the resulting layers was studied (Figure 3). The substrate temperature varied in the range from 350 to 550 °C at the constant plasma power of 30 W.

Figure 3. The influence of the substrate temperature (c-sapphire) on the surface morphology of the gallium oxide films.

In this case, we deliberately used the minimum required plasma power to exclude the effect of annealing of gallium oxide structures from the plasma discharge and to observe only the effects associated with the substrate temperature. According to the AFM results, the surface of the Ga₂O₃ films is formed by crystallites which are randomly located in space, but are equally oriented relative to each other. The surface of the Ga₂O₃ sample deposited at 350 °C includes triangular crystallites. At the substrate temperature of 450 °C crystallites with a quadrangular shape are formed. The increase of the substrate temperature to 550 °C leads to both a significant increase in the size of the structural units and the surface roughness. The distribution of Ga₂O₃ crystallites according to the sizes for the first and the third deposited films is bimodal. That is, it can be assumed that the increase in the temperature from 350 to 450 °C leads the phase transition, the crystallites change both the shape and the size, however their distribution reflects the unimodal behaviour [26]. In the case of the layer obtained at 550 °C, the size of Ga₂O₃ crystallites becomes much larger.

To sum up, some preliminary conclusions may be formulated comparing the layers modified by the increase of the plasma power and by the rise of the substrate temperature. In the first case, the enlargement of crystallinity is reached via improvement of the structure quality – the sizes of the structural units get smaller and the surface gets smoother. In the second case, the enlargement of
crystallinity is obtained due to the growth of the structural fragments in size and the increase of the quantity of the lattice’s defects.

3.4. Results of X-ray phase analysis of the films grown at different plasma powers on the c-sapphire substrate

The results of measuring the crystallinity degree of gallium oxide thin films obtained at different plasma discharge powers by the X-ray phase analysis are shown in Figure 4. Even at the minimum plasma power, we can clearly distinguish a peak at 38.90°, corresponding to ε-Ga₂O₃, which in some scientific literature is considered as a β-phase with a large number of dangling -Ga-O- bonds [27-29]. The increase in the plasma power up to 30 W leads to the increase in the intensity of this peak; this corresponds to the growth of pyramidal fragments of the crystalline structure in the AFM images presented above in Figure 2. In case of the samples obtained in the plasma at powers above 30 W three diffraction peaks located at 18.95°, 38.40°, and 59.19° and corresponding to the structural fragments of β-Ga₂O₃ appear. Namely, at the plasma power of 50 W, instead of the peak near 38.90°, a diffraction maximum appeared on the X-ray diffraction patterns of the samples at 38.40°, the intensity of the diffraction maximum noticeably increased with the further increase of the plasma power. This conforms to the AFM results, when the formation of cubic crystallites related to β-Ga₂O₃ was observed. However, the weak diffraction maximum at 18.95° is hardly noticeable; this is probably due to the insufficient thickness of the layers. The analysis of the change in the intensity of the diffraction peak at 59.19° turned out to be impossible due to the hardware limitations of the used instrument base.

![XRD results of gallium oxide films obtained on c-sapphire at different plasma powers.](image)

Nevertheless, the data obtained allow to conclude that the increase in the values of the power supplied to the discharge results in both the significant increase in the degree of crystallinity of the gallium oxide structures and the uniformity of the crystalline structure; it is evidenced by the decrease in the noise intensity and the sharp increase in the peak referring to crystalline β-phase of gallium oxide [30].

3.5. XRD results of films obtained at different c-sapphire substrate temperatures

The results of X-ray diffraction studies of gallium oxide films obtained at different substrate temperatures and a constant plasma power (30 W) are shown in Figure 6. The sample, deposited at the substrate temperature 350 °C, manifests itself as ε-phase of Ga₂O₃ (peak at 38.90°). The additional peaks, observed at 41.66 and 44.1, refer to the sapphire substrate and the aluminium measurement cell, respectively. However, as the substrate temperature rises to 450 °C, crystallization and growth of gallium oxide particles into the monoclinic β-modification with the space group C2/m occur; it is evidenced by the diffraction reflection maxima near 30, 31.74, 35.18, and 38.40°. The further increase...
of the substrate temperature to 550 °C leads to the increase in the intensity of β-Ga$_2$O$_3$ peaks; this corresponds to the increase in the size of cubic crystallites in AFM images (Figure 5).

![Figure 5. XRD patterns of the films obtained at different c-sapphire substrate temperatures (350 °C - triangular crystallites, 450 °C - square crystallites, 550 °C - square coarse crystallites).](image)

Thus, based on the AFM and XRD data, it can be assumed that the plasma-chemical method allows achieving structural perfection and phase homogeneity of the final β-gallium oxide material either due to a traditional increase of the substrate temperature, resulting in the formation of the most thermodynamically stable polycrystalline β-phase of gallium oxide, or by means of increasing the power of the plasma discharge.

4. Conclusion
A novel plasma-chemical method of heteroepitaxial synthesis of β-Ga$_2$O$_3$ thin films has been developed. Optical emission diagnostics of the plasma discharge was carried out at various ratios of substances in the gas phase, as well as at various values of the generator power. The influence of the substrate temperature and discharge power on the structure of β-Ga$_2$O$_3$ layers has been studied. It is shown that it is possible in principle to obtain epitaxial layers in the conditions of heteroepitaxial growth using the proposed method. It has been found out that the increase of the plasma power at relatively low substrate temperatures practically does not cause a sharp growth of structure-forming fragments. Instead, the ordered growth of gallium oxide occurs immediately in the form of the β-phase we need, while the necessity of additional annealing disappears by itself.

5. References
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