Rev. Adv. Mater. Tech. vol. 3 no 4 (2021) 7–12
DOI: 10.17586/2687-0568-2021-3-4-7-12

# Spray-Pyrolysis Fabrication and Quality Study of β-$Ga_2O_3$ Thin Films

**D.I. Panov[1], Z. Xi[1], V.A. Spiridonov[1], L.V. Azina[1], R.K. Nuryev[1], N.D. Prasolov[2], L.A. Sokura[1], D.A. Bauman[1] and V.E. Bougrov[1]**

[1] ITMO University, Kronverkskiy pr., 49, lit. A, Saint Petersburg, 197101, Russia
[2] Ioffe Institute, Politekhnicheskaya str., 26, Saint Petersburg 194021, Russia

*Received: December 17, 2021*

**Abstract.** In this paper, we report on the successful fabrication of β-$Ga_2O_3$ thin films by spray-pyrolysis technique. We provide the data on the dependence of the quality of the β-$Ga_2O_3$ films on the regimes and parameters of fabrication. Scanning electron microscopy, atomic force microscopy and optical spectroscopy are used to analyze film properties. X-ray diffraction phase analysis of the films after heat treatment at 900°C confirms the formation of β-$Ga_2O_3$ crystallites.

## 1. INTRODUCTION

Gallium oxide ($Ga_2O_3$), an emerging transparent semiconducting oxide, has attracted much attention in recent years because of its ultra-wide bandgap (~4.8 eV), high breakdown electric field (> 8 MV/cm), and relatively high electron mobility (~150 $cm^2$/V·s) [1–4]. $Ga_2O_3$ has several polymorphic forms according to available reports, namely crystalline phases with rhombohedral (α-$Ga_2O_3$), monoclinic (β-$Ga_2O_3$), defective spinel (γ-$Ga_2O_3$), cubic (δ-$Ga_2O_3$) and orthorhombic (ε-$Ga_2O_3$) structures [1,2]. Another transient polymorph (κ-$Ga_2O_3$) has also been recently reported [5]. β-$Ga_2O_3$ is the most thermodynamically stable phase among them. Nowadays, $Ga_2O_3$ finds promising applications in power electronic devices, optoelectronic devices, sensing systems, memory devices, deep ultraviolet transparent conductive oxide electrodes, photocatalysts, etc. [1,2,6–8].

There is an urgent demand to develop high-quality $Ga_2O_3$ films. Gallium oxide films can be prepared by metal organic chemical vapor deposition (MOCVD) [9], pulsed laser deposition (PLD) [10], radio frequency magnetron sputtering (RFMS) [11,12], halide vapor phase epitaxy (HVPE) [13], and sol-gel methods [14,15]. Among the listed techniques, the sol-gel method has advantages for the fabrication of $Ga_2O_3$ thin films because of simple equipment, convenient operation, no vacuum environment, and low costs [14,16]. It has been reported that sol-gel methods can operate with spin coating [14], dip coating [17], and spray coating (spray-pyrolysis) [18]. In our work, the spray coating method was used to fabricate $Ga_2O_3$ films. This method is easier and more efficient for obtaining uniform thin films.

## 2. EXPERIMENTAL SETUP AND METHODOLOGY

$Ga_2O_3$ films were prepared on silica glass ($SiO_2$) substrates by the spray-coating method. To obtain solution for preparing gallium oxide film, gallium nitrate [$Ga(NO_3)_3 \cdot 8H_2O$] (99.9%) was dissolved in ethylene glycol [$C_2H_6O_2$] (99.5%) with addition of monoethanolamine [$C_2H_7NO$] (99.5%) as stabilizer. Solution was stirred at 60 °C for 60 minutes. The molarity

Corresponding author: D.I. Panov, e-mail: dmitriipnv@gmail.com

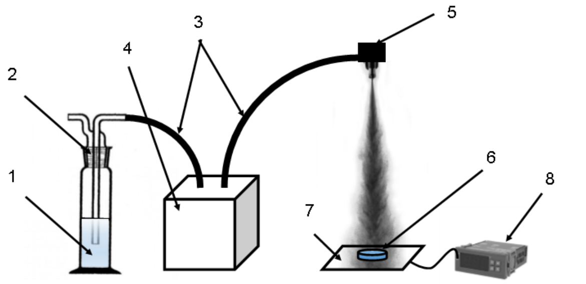


**Fig. 1.** Schematics of spray-pyrolysis gallium oxide application unit.

of gallium nitrate and ethylene glycol was 0.25 mol/l while the molar ratio of gallium nitrate and monoethanolamine was 3:1. Silica glass substrates were ultrasonically cleaned with isopropyl alcohol for 10 minutes.

The experimental setup for the preparation of $Ga_2O_3$ thin films by spray pyrolysis is schematically shown in Fig. 1. Here the solution (1) is pumped from the vessel (2) through silicone pipes (3) by the high-pressure pump (4) to the spraying nozzle with an outlet diameter of 0.1 mm (5). The spray from the nozzle is deposited on the substrate (6) located on the heated table (7) that is connected to the temperature control system (8). The distance from the nozzle to the substrate was about 30 cm.

The stages of spraying procedure are explained in Fig. 2. Two substrates were placed on the heated stage and the colloidal solution was sprayed. Each layer was deposited on the substrate at 120 °C for 2 seconds. Then it was dried at 120 °C for 120 seconds to get rid of excess water and carbon dioxide. After layer deposition, one of the samples was placed in the preheated muffle furnace and treated at 500 °C for 5 minutes. The process was repeated until 30 layers have been deposited. The last step was the annealing of the sample at 900 °C for 120 minutes for obtaining β-phase $Ga_2O_3$ films. All the deposition and annealing processes were carried out in air.

The morphology of the obtained films was characterized by atomic force microscopy (AFM) technique using Dimension 3100 microscope in dynamic contact mode. Scanning electron microscopy (SEM) images of the films were obtained with TESCAN Mira 3 microscope with FEG Schottky electron emission source. The X-ray diffraction (XRD) data were obtained using the Rigaku Ultima IV X-ray diffractometer. The diffraction database International Center for Diffraction Data (ICDD) PDF-2 (2008) was used to interpret diffraction reflexes. The optical properties were studied in the 200–1000 nm range by optical spectrometer (AvaSpec-ThinFilm).

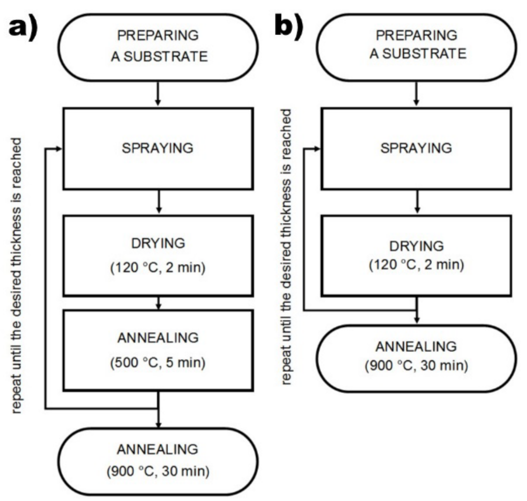


**Fig. 2.** Gallium oxide film preparation by spraying method; a) without pre-annealing at 500 °C, b) with pre-annealing at 500 °C.

## 3. RESULTS AND DISCUSSION

The main goal of the experiments was to investigate the effect of preliminary annealing at 500 °C on the quality and optical properties of the fabricated gallium oxide films. The work also aimed to minimize the number of cracks, inclusions, and to reduce the average roughness of the β-$Ga_2O_3$ films. To obtain the detailed information about the surface morphology, the samples were examined before and after the final 900 °C heat treatment. Samples that were not initially pre-annealed at 500 °C (Fig. 3a) have a significant number of cracks and ruptures in the resulting film. Samples pre-annealed at 500 °C show a uniform structure with no cracks or additional defects (Fig. 3b).

After final annealing of samples at 900 °C for 120 minutes the following picture is observed: at film transition from amorphous state to β-$Ga_2O_3$ change in morphology of fabricated surface occurs, in particular, the large number of cracks and delaminations are observed in samples that have not passed the preliminary annealing (Fig. 4a). The samples that had the preliminary annealing at 500 °C show a uniform structure without visible cracks and delaminations of the resulting layer (Fig. 4b). Films that were not annealed at 900 °C showed no diffraction peaks and therefore were in an amorphous or X-ray amorphous state.

To study the surface roughness of the films and the effect of additional annealing at 500 °C on their morphology, an AFM analysis was carried out. The scanning area was 10×10 µm. The data on the mean square and mean arithmetic roughness of the obtained gallium oxide thin films are presented in Table 1.

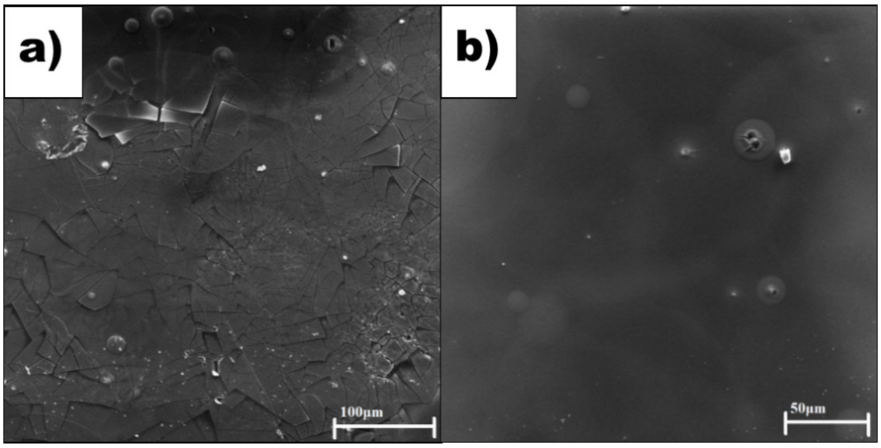


**Fig. 3.** SEM images of amorphous gallium oxide film obtained by spray-pyrolysis: a) without pre-annealing at 500 °C, b) with pre-annealing at 500 °C.

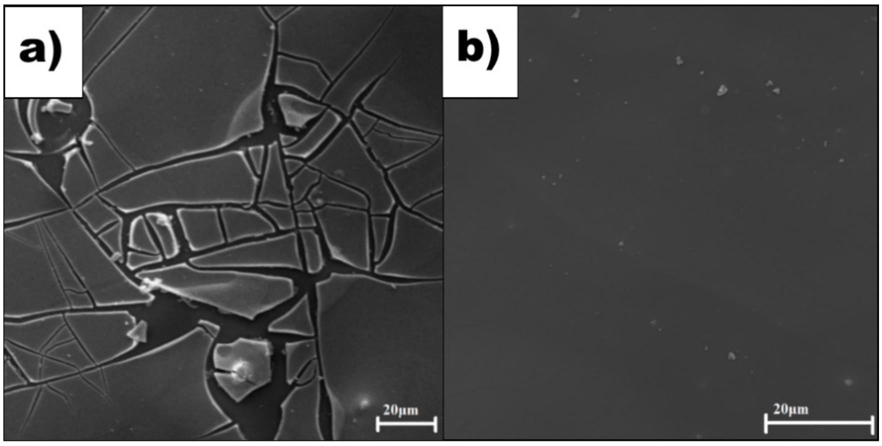


**Fig. 4.** SEM images beta gallium oxide film obtained by spray-pyrolysis with 900 °C annealing: a) without pre-annealing at 500 °C, b) with pre-annealing at 500 °C.

Comparing the AFM data for samples that were not subjected to final annealing at 900 °C, there is a significant increase in the roughness of the fabricated thin film, which is demonstrated by the results of SEM and AFM. Their morphology is associated with a significant number of cracks and delamination of the thin film, related to poor adhesion at the stage of deposition, as well as to remains of organics in the interlayer space of the resulting film. However, it should be noted that the samples that had the final 900 °C heat treatment show slight variation in the roughness data, but according to SEM data the structure of the samples that did not have the 500 °C pre-anneal is significantly worse compared to the pre-annealed samples. Many defects are observed on the surface of samples without pre-annealing at 500 °C. The films without the 500 °C pre-annealing show a strong roughness lateral gradient comparing the samples before and after the 900 °C heat treatment. The decrease in roughness from 15 nm to 2.11 nm indicates the final removal of organics from the interlayer space and the formation of β-$Ga_2O_3$ film. On the other hand, the roughness lateral gradient is less than 0.5 nm for films pre-annealed at 500 °C, indicating the

**Table 1.** Summary table of AFM study results of sample roughness.

| Type of sample treatment | Mean square roughness, nm | Mean arithmetic roughness, nm |
|---|---|---|
| no treatment | 15 | 7.01 |
| 500 °C pre-annealing | 1.86 | 0.975 |
| 900 °C annealing | 2.11 | 1.26 |
| 500 °C pre-annealing and 900 °C annealing | 1.40 | 0.981 |

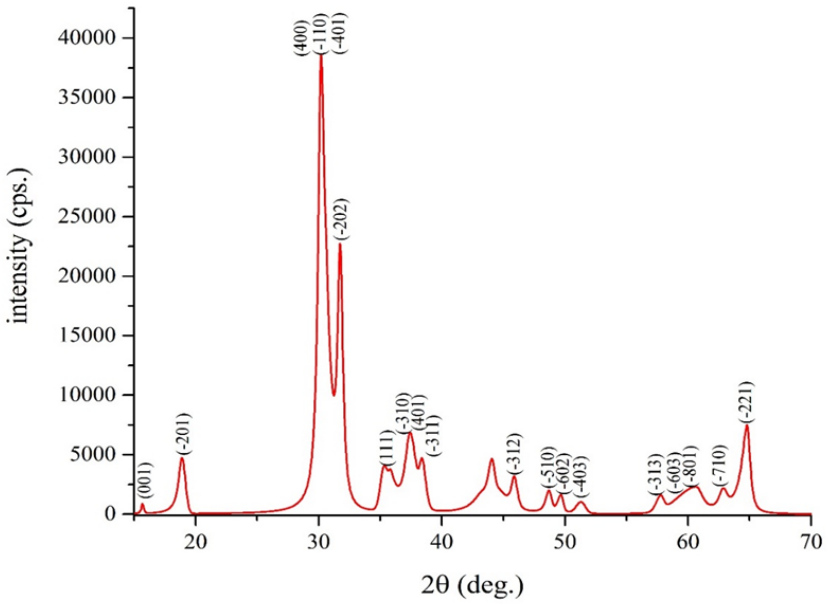


**Fig. 5.** X-ray diffraction (XRD) pattern of obtained thin films of $Ga_2O_3$ by spray-pyrolysis method, after annealing at 900 °C, indexed in comparison to ICDD data (PDF 00-041-1103).

absence of organics in the interlayer space. After the 900 °C annealing, film rearrangement is observed: growth of β-$Ga_2O_3$ crystallites without formation of additional defects.

XRD phase analysis data showed that in the samples without final 900 °C annealing there are no crystalline phases, this suggests the amorphousness of the initially obtained film. However, diffraction peaks corresponding to β-$Ga_2O_3$ (Fig. 5) appeared in the samples after the 900 °C heat treatment, indicating that the film was rearranged and transformed to the crystalline state.

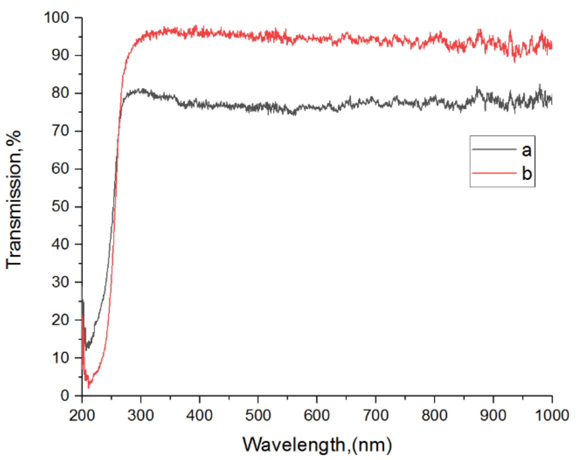


**Fig. 6.** Optical transmission spectra for samples after final annealing at 900 °C: a) without pre-annealing at 500 °C, b) with pre-annealing at 500 °C.

According to the optical spectroscopy data (Fig. 6), additional 500 °C heat treatment led to an increase in optical transparency in the wavelength range of 300–1000 nm and an increase in optical absorption in the range of 200–250 nm. In the 300–1000 nm wavelength range less scattering is observed at both the air/film and film/substrate interfaces for samples fabricated with the 500 °C pre-annealing. This effect is due to the presence of cracks and surfaces with rough morphology in the samples that were not pre-annealed at 500 °C. The same effect is observed for 200–250 nm range. Due to the occurrence of cracks in the resulting films without pre-annealing at 500 °C, the absorption intensity in the UV range decreases.

## 4. CONCLUSION

Results on the fabrication of β-$Ga_2O_3$ films on silica glass substrate by spray-pyrolysis technique have been reported in this work. It has been demonstrated that the quality of the obtained gallium oxide films can be improved by the pre-annealing treatment at 500 °C. Surface morphology data have been obtained by AFM giving the roughness ~1 nm for the pre-annealed films. Qualitative characteristics of gallium oxide films have been studied by SEM analysis. According to SEM data, the films obtained with pre-annealing at 500 °C have better quality, notably they do not have cracks in the film structure. The study of optical transmission spectra showed higher transmittance for samples with pre-annealing at 500 °C in the wavelength range of 300–1000 nm. XRD phase analysis of the fabricated films has demonstrated no diffraction peaks for the films after the pre-annealing stage, i.e., indicating their amorphousness. After 900 °C final annealing, all samples have demonstrated peaks that are caused by β-$Ga_2O_3$ crystalline phase.

We conclude that pre-annealing (at 500 °C) has a significant effect on the quality of spray-pyrolysis fabricated gallium oxide films that transform to crystalline β-phase state as a result of the final treatment at high temperature (900 °C).

## ACKNOWLEDGEMENTS

The authors are grateful to Prof. A.E. Romanov and Dr. A.M. Smirnov for valuable discussions and comments that helped in the preparation of the manuscript. This work was conducted as part of the research program of the scientific school "Theory and practice of advanced materials and devices of optoelectronics and electronics" (scientific school 5082.2022.4).

## REFERENCES

[1] S.I. Stepanov, V.I. Nikolaev, V.E. Bougrov and A.E. Romanov, *Gallium oxide: properties and applications – a review*, Rev. Adv. Mater. Sci., 2016, vol. 44, pp. 63–86. https://www.ipme.ru/e-journals/RAMS/no_14416/06_14416_stepanov.pdf

[2] S.J. Pearton, J. Yang, P.H. Cary, F. Ren, J. Kim, M.J. Tadjer and M.A. Mastro, *A review of $Ga_2O_3$ materials, processing, and devices*, Appl. Phys. Rev., 2018, vol. 5, no. 1, art. no. 011301. https://doi.org/10.1063/1.5006941

[3] Z. Galazka, *β-$Ga_2O_3$ for wide-bandgap electronics and optoelectronics*, Semicond. Sci. Technol., 2018, vol. 33, no. 11, art. no. 113001. https://doi.org/10.1088/1361-6641/aadf78

[4] M. Yu, C. Lv, J. Yu, Y. Shen, L. Yuan, J. Hu, S. Zhang, H. Cheng, Y. Zhang and R. Jia, *High-performance photodetector based on sol–gel epitaxially grown α/β $Ga_2O_3$ thin films*, Mater. Today Commun., 2020, vol. 25, art. no. 101532. https://doi.org/10.1016/j.mtcomm.2020.101532

[5] H.Y. Playford, A.C. Hannon, E.R. Barney and R.I. Walton, *Structures of uncharacterised polymorphs of gallium oxide from total neutron diffraction*, Chem. Eur. J., 2013, vol. 19, no. 8, pp. 2803–2813. https://doi.org/10.1002/chem.201203359

[6] Z. Hu, K. Nomoto, W. Li, Z. Zhang, N. Tanen, Q.T. Thieu, K. Sasaki, A. Kuramata, T. Nakamura, D. Jena and H.G. Xing, *Breakdown mechanism in 1 kA/cm$^2$ and 960 V E-mode β-$Ga_2O_3$ vertical transistors*, Appl. Phys. Lett., 2018, vol. 113, no. 12, art. no. 122103. https://doi.org/10.1063/1.5038105

[7] Z. Galazka, K. Irmscher, R. Uecker, R. Bertram, M. Pietsch, A. Kwasniewski, M. Naumann, T. Schulz, R. Schewski, D. Klimm and M. Bickermann, *On the bulk β-$Ga_2O_3$ single crystals grown by the Czochralski method*, J. Cryst. Growth, 2014, vol. 404, pp. 184–191. https://doi.org/10.1016/j.jcrysgro.2014.07.021

[8] X. Chen, F. Ren, S. Gu and J. Ye, *Review of gallium-oxide-based solar-blind ultraviolet photodetectors*, Photonics Res., 2019, vol. 7, no. 4, pp. 381–415. https://doi.org/10.1364/PRJ.7.000381

[9] D.A. Bauman, A.I. Borodkin, A.A. Petrenko, D.I. Panov, A.V. Kremleva, V.A. Spiridonov, D.A. Zakgeim, M.V. Silnikov, M.A. Odnoblyudov, A.E. Romanov and V.E. Bougrov, *On improving the radiation resistance of gallium oxide for space applications*, Acta Astronaut., 2021, vol. 180, pp. 125–129. https://doi.org/10.1016/j.actaastro.2020.12.010

[10] A. Goyal, B.S. Yadav, O.P. Thakur, A.K. Kapoor and R. Muralidharan, *Effect of annealing on β-$Ga_2O_3$ film grown by pulsed laser deposition technique*, J. Alloys Compd., 2014, vol. 583, pp. 214–219. https://doi.org/10.1016/j.jallcom.2013.08.115

[11] X. Zhang, D. Jiang, M. Zhao, H. Zhang, M. Li, M. Xing, J. Han and A.E. Romanov, *The effect of annealing temperature on $Ga_2O_3$ film properties*, J. Phys. Conf. Ser., 2021, vol. 1965, no. 1, art. no. 012066. https://doi.org/10.1088/1742-6596/1965/1/012066

[12] Y. Zhao, *Preparation and properties of Zn-doped β-$Ga_2O_3$ films*, Acta Photonica Sinica, 2012, vol. 41, no. 10, pp. 1242–1246. https://doi.org/10.3788/gzxb20124110.1242

[13] A.V. Kremleva, Sh.Sh. Sharofidinov, A.M. Smirnov, E. Podlesnov, M.V. Dorogov, M.A. Odnoblyudov, V.E. Bougrov and A.E. Romanov, *Growth of thick gallium oxide on the various substrates by halide vapor phase epitaxy*, Mater. Phys. Mech., 2020, vol. 76, no. 2, pp. 164–171. https://doi.org/10.18720/MPM.4422020_2

[14] Y. Zhu, X. Xiu, F. Cheng, Y. Li, Z. Xie, T. Tao, P. Chen, B. Liu, R. Zhang and Y.-D. Zheng, *Growth and nitridation of β-$Ga_2O_3$ thin films by*

*Sol-Gel spin-coating epitaxy with post-annealing process*, J. Sol-Gel Sci. Technol., 2021, vol. 100, no. 1, pp. 183–191. https://doi.org/10.1007/s10971-021-05629-4

[15] L.B. Cheah, R.A.M. Osman and P. Poopalan, *$Ga_2O_3$ thin films by sol-gel method its optical properties*, AIP Conf. Proc., 2020, vol. 2203, no. 1, art. no. 020028. https://doi.org/10.1063/1.5142120

[16] H. Shen, Y. Yin, K. Tian, K. Baskaran, L. Duan, X. Zhao and A. Tiwari, *Growth and characterization of β-$Ga_2O_3$ thin films by sol-gel method for fast-response solar-blind ultraviolet photodetectors*, J. Alloys Compd., 2018, vol. 766, pp. 601–608. https://doi.org/10.1016/j.jallcom.2018.06.313

[17] Y. Ohya, J. Okano, Y. Kasuya and T. Ban. *Fabrication of $Ga_2O_3$ thin films by aqueous solution deposition*, J. Ceram. Soc. Jpn., 2009, vol. 117, no. 1369, pp. 973–977. https://doi.org/10.2109/jcersj2.117.973

[18] N. Winkler, R.A. Wibowo, W. Kautek, G. Ligorio E.J.W. List-Kratochvil and T. Dimopoulos, *Nanocrystalline $Ga_2O_3$ films deposited by spray pyrolysis from water-based solutions on glass and TCO substrates*, J. Mater. Chem. C, 2018, vol. 7, no. 1, pp. 69–77. https://doi.org/10.1039/C8TC04157A