Gallium oxide thin films synthesis in different phase composition by gallium interaction with oxygen in oxygen-hydrogen plasma on silicon substrates

L A Mochalov, A A Logunov and I O Prokhorov

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

*igorprokhorov1998@yandex.ru

Abstract. A modern synthesis method by plasma-chemical deposition of gallium oxide layers was developed. High-purity gallium was utilized as the source of gallium for moving by hydrogen flow into the reaction zone for interaction with oxygen in plasma discharge. Low temperature non-equilibrium RF (40MHz) plasma discharge was utilized for initiation interactions between precursors at a pressure of 0.1 Torr. The optical emission spectroscopy was used to assess the main excited particles formed in the gas phase. The paper researches the dependence of properties of the solid phase, grown on the silicon substrate, on the experimental parameters.

1. Introduction

Currently, a lot of scientists try to develop a new modern analogue to silicon in the manufacturing of electronic components. Ga2O3 thin films can be utilized instead of silicic chip in various electronic devices such as transistors, emitters, antireflective coatings [1-3]. Ga2O3 layers may be obtaining by many ways [4-9]. Hetero epitaxial amorphous and polycrystallineβ-Ga2O3, which are usually of a not enough structural quality, may be grown by different synthesis methods [10-12]. In spite of utilizing different crystalline materials wafers and annealing after obtaining at high temperatures, FWHM values of the rocking curves are typically larger than 1000 arc sec. Moreover, the usage of MOC or gallium chlorides as a gallium source of volatile gallium derivatives is a common task of the available semiconductors obtaining methods. In the resulting thin films, due to the use of volatile precursors of Ga, these components always remain, which deteriorate their characteristics and contaminate materials.

Developing a new approach to a hetero epitaxial growth of the Ga2O3 epitaxial layers on Si wafers using elemental high-purity gallium as a precursor in the oxygen-hydrogen low temperature non-equilibrium plasma discharge is the aim of this research.
2. Experiment
The experiments were realized on the plasma-chemical installation which was shown in minutely in [13-17]. The experimental setup included a system of gas supply, a high-purity quartz glass reactor for plasma-chemical interaction which had the inner diameter 25 mm, and a system for pumping. The system of gas supply was consisted of gas pressure regulators, controllers of mass flow and a vacuum stainless steel tubing vacuum flange. The gas supply system was joined with plasma-chemical reactors by the vacuum flange, and used as the loading of high-purity gallium source. The reactor’s part with the charged gallium was surrounded by outer heater. The rest of the reactor was equipped with the external inductor for the ignition of the plasma discharge. A RF generator was applied with a matching unit at frequency in 40 MHz. The substrates were perpendicularly located to the flow and held by a unique holder right into the zone of plasma discharge. H₂ of high-purity was utilized as carrier-gas, being breezed with an invariable speed across the gallium source. O₂ of high-purity was delivered right into the zone of plasma discharge. 31 ml/min at the overall pressure in the system 2×10⁻¹ Torr was the total consumption. The gallium source’s temperature was kept constant 760 °C; silicon was a material for the wafers with a size 11x11 mm. The wafers temperature was invariably 360 °C.

3. Results and discussion

3.1. Ga-O₂-H₂ optical emission spectroscopy with the invariable relation H₂:O₂ = 2:1 at various power of plasma discharge
The optical emission spectroscopy was showed effect of plasma power on the forming of excited particles in the gas phase of the source substances, as it was shown in [18-20]. Gallium-oxygen-hydrogen plasma emission spectra of the mixture at different generator energy from 100 to 30 W, detected in the band of 355-1055 nm which are demonstrated in Figure 1.

![Figure 1. Ga + H₂O₂ emission spectra in plasma of mixture (2:1) at different energy input. This normalized spectra at the generator power 30 and 100W is the insertion.](image_url)

In the band of 440-910 nm were identified the atomic and molecular lines of atomic and molecular H₂ and O₂. Gallium Ga (I) atoms with high-intensity emissive lines are kept at 417.2 nm and 403.3 [18], Ga (II) excited states have a weak line which are located at 779.31 nm. The intensity of the all the emissive lines in the spectrum increases with the increase the intensity of plasma power. The Figure 1 in the insertion shows the normalized spectra of plasma at the 30 and 100 W power of generator. Ga (I) atomic lines at 403.32, 417.21 nm and the molecular hydrogen lines hydrogen (I) at 472.32, 482.31, 639.51 nm relative intensity significantly increases as well. We previously observed with the hydrogen excess at the discharge power more than 71 W [21], H₂ etching of the growing gallium oxide layer by the hydrogen-oxygen plasma happens. The decrease of this assumption was confirmed by in the film growth speed [22]. It was shown that when the power of generator is less than
31 W the layers of polycrystalline granular with a high asperity of surface grow on the wafer. So, 51-71 W plasma power of discharge in the conditions and technology of our experiment was optimal.

3.2. Ga$_2$O$_3$ layers’ morphology and surface AFM research
The crystalline cubic crystallites of the $\beta$-Ga$_2$O$_3$ phase were immediately formed on the silicon surface (Figure 2) with the average size of structural parts $380\times10^2$ nm$^2$ with the coefficient of variation of 31 % and the surface roughness of $X = 4.15$ nm, $Z = 15.88$ nm (Figure 2) at the minimum power of plasma 20 W.

| Plasma Power | Roughness |
|--------------|-----------|
| 20 W         | $X = 4.15$ nm, $Z = 15.88$ nm |
| 30 W         | $X = 4.42$ nm, $Z = 14.35$ nm |
| 50 W         | $X = 2.24$ nm, $Z = 13.43$ nm |
| 70 W         | $X = 1.02$ nm, $Z = 10.57$ nm |

$^*$R$_a$ – average roughness; R$_z$ – height of the profile roughness

**Figure 2.** Plasma power influence on the morphology of the Ga$_2$O$_3$ deposited on the crystalline silicon wafers.

An increase in the plasma power, first to 30W and then up to 50W, led to decrease in both crystallite size (> 34 % (Figure 3)) and the film surface roughness up to $X = 2.24$ nm, $Z = 13.43$ nm.
The gradual increase of the plasma discharge power usually led to the change in the relaxation conditions of the excited particles that form the structural elements of the deposited solid phase. Then, unlike a series of synthesis with the c-sapphire substrate [23-27], the ε-Ga$_2$O$_3$ phase usually is not prepared. The β-Ga$_2$O$_3$ polymorph was grown, this structure is like epitaxial in its characteristics. It was done at the maximum plasma power 70 W [28]. The roughness of surface’s morphology was only $X = 1.02$ nm at $Z = 10.57$ nm. Speed of film growth was also estimated by the stepped method, the AFM method. It was 11-49 nm/h.

So, further development of the method to fully control this synthesis process. In addition, the formation of hetero epitaxial layers on silicon substrates is possible, despite the differences in the crystal lattice parameters between single-crystal and β-Ga$_2$O$_3$.

**Figure 3.** The influence of power of plasma on the distribution of crystallites on the surface of thin gallium oxide films by size.

3.3. The results of the X-ray phase analysis of the films grown at different plasma power on silicon substrates

X-ray phase analysis demonstrates the results of measurement of the crystallinity degree of Ga$_2$O$_3$ thin films obtaining at various plasma discharge power. They are shown in Figure 4.

The film obtaining at the low plasma power discharge has a broadening of the base line. The results of the this X-ray may be easily explained by a structural disorder of the crystalline fragments forming the lattice [29, 30]. Even at the low plasma energy at 38.401° the β-Ga$_2$O$_3$ has a neatly noticeable peak corresponding to the growth of the cubic fragments of the crystalline structure in the AFM images.
presented above in Figure 2. The increase in plasma power leads to the increase of the peak intensity with a simultaneous decrease of the baseline width.

This X-ray agree with the AFM results. The ordering of cubic crystallites was found out. However, a weak diffraction maximum at 18.951° is hardly noticeable. It is may be connected with an insufficient thickness of the layers. The intensity change analysis of the diffraction peak at 59.192° was impossible due to the hardware limitations of the used instrument base.

Nevertheless, the obtained data allow concluding that the increase of the plasma power results in the significant increase of the gallium oxide layers’ homogeneity.

![X-ray diffraction patterns of the Ga\(_2\)O\(_3\) films obtained on the silicon substrates at various plasma power.](image)

**Figure 4.** X-ray diffraction patterns of the Ga\(_2\)O\(_3\) films obtained on the silicon substrates at various plasma power.

3.4. *The optical properties of the obtained materials*

The breadth of the optical band gap was appreciated by the Tauc method. The curves are presented in the insertion to Figure 5. With the increase of the plasma discharge power the optical band gap increases from 4.251 to 4.41 eV. It again indicates the decrease of the structural defects in the layer with the higher structural order and its parameters approximation to the epitaxial.

![The transmission spectra of the Ga\(_2\)O\(_3\) thin films depending on the plasma’s generator power for utilizing Tauc method to calculate optical band gap.](image)

**Figure 5.** The transmission spectra of the Ga\(_2\)O\(_3\) thin films depending on the plasma’s generator power for utilizing Tauc method to calculate optical band gap.

4. **Conclusions**

A modern method of plasma-chemical hetero epitaxial obtaining of gallium oxide thin films utilizing as the precursor only high-purity elemental Ga which was supplied by the hydrogen flow into the H\(_2\)-O\(_2\)RF plasma discharge reaction zone was developed. Plasma discharge in reaction zone at various
values of the generator power was researched by optical emission spectroscopy in the band of 355-1055. The discharge power influence on the structure and optical properties of β-gallium oxide layers has been studied. As a result, it was found that with an increase in the plasma power at relatively low substrate temperatures, it is possible to obtain epitaxial layers and they have a good quality in terms of surface morphology, purity, and structural homogeneity.

5. References
[1] Granqvist C G 2006 Nat. Mater. 5 89
[2] Fleischer M and Meixner H 1991 Sens. Actuators B Chem. 4 437
[3] Liu Z, Li P-G, Zhi Y-S, Wang X-L, Chu X-L and Tang W-H 2019 Chin. Phys. B 28 017105
[4] Zatsepin D A, Boukhvalov D W, Zatsepin A F, Kuznetsova Y A, Gogova D S, Shur V Y, Esin A A 2018 Superlattices and Microstructures 120 90
[5] Marwoto P, Sugianto S and Wibowo E 2012 J. Theor. Appl. Phys. 6 17
[6] Minami T 2003 Solid. State. Electron. 47 2237
[7] Jinno R, Chang C S, Onuma T, Cho Y, Ho S-T, Rowe D, Cao M C, Lee K, Protasenko V, Schlom D G, Muller D A, Xing H G and Jena D 2021 Sci. Adv. 7 eabds5891
[8] Marie P, Portier X and Cardin J 2008 Phys. Status Solidi A 205 1943
[9] Kukushkin S A, Osipov A V, Osipova E V, Feoktistov N A, Nikolaev V I, Pechnikov A I 2016 Phys. Solid State 58 1876
[10] Binions R, Carmalt C J, Parkin I P, Pratt K F E and Shaw G A 2004 Chem. Mater. 16 2489
[11] Ortiz A, Alonso J C, Andrade E and Urbiola C 2001 J. Electrochem. Soc. 148 F26
[12] Murakami H, Nomura K, Goto K, Sasaki K, Kawara K, Thieu Q T, Togashi R, Kumagai Y, Higashiwaki M, Kuramata A, Yamakoshi S, Monemar B and Koukitu A 2015 Appl. Phys. Express 8 015503
[13] Mochalov L, Logunov A, Kitnis A, Prokhorov I, Kovalev A, Yunin P, Gogova D and Vorotyntsev V 2020 Sep. Purif. Technol. 238 116446
[14] Mochalov L, Logunov A, Gogova D, Zelentsov S, Prokhorov I, Starostin N, Letnianchik A and Vorotyntsev V 2020 Opt. Quantum Electron. 52 510
[15] Mochalov L, Logunov A, Sazanova T, Gogova D, Zelentsov S, Yunin P, Prokhorov I, Malyshev V and Vorotyntsev V 2020 Int. Conf. on Transparent Optical Networks 2020-July 9203286
[16] Mochalov L, Logunov A, Sazanova T, Kulikov A, Rafailov E, Zelentsov S and Vorotyntsev V 2020 Int. Conf. on Transparent Optical Networks 2020-July 9203466
[17] Logunov A, Mochalov L, Gogova D and Vorotyntsev V 2019 Int. Conf. on Transparent Optical Networks 2019-July 830431
[18] Mochalov L, Logunov A, Kitnis A and Vorotyntsev V 2020 Plasma Chem. Plasma Process. 40 407
[19] Mochalov L, Logunov A, Markin A, Kitnis A and Vorotyntsev V. 2019 Mater. Res. Express 6 126436
[20] Mochalov L, Logunov A, Markin A, Kitnis A and Vorotyntsev V 2020 Opt. Quantum Electron. 52 197
[21] Mochalov L, Logunov A and Vorotyntsev V 2021 Sep. Purif. Technol. 258 118001
[22] Cox R A and Coker G B 1983 J. Phys. Chem. 87 4478
[23] Harwood M H, Burkholder J B, Hunter M, Fox R W and Ravishankara A R 1997 J. Phys. Chem. A 101 853
[24] Jenkin M E, Cox R A and Candelend D E 1985 J. Atmos. Chem. 2 359
[25] Laszlo B, Kurylo M J and Huie R E 1995 J. Phys. Chem. 99 11701
[26] Bloss W J, Rowley D M, Cox R A and Jones R L 2001 J. Phys. Chem. A 105 7840
[27] Gómez Martí n J C, Spietz P and Burrows J P 2007 J. Phys. Chem. A 111 306
[28] Gómez Martí n J C, Ga'tvezO, Baeza-Romero M T, Ingham T, Plane J M C and Blitz M A 2013 Phys. Chem. Chem. Phys. 15 15612
[29] Stepanov S I, Nikolaev V I, Bougrov V E and Romanov A E 2016 Rev. Adv. Mater. Sci. 44 63
[30] Mastro M A, Kuramata A, Calkins J, Kim J, Ren F and Peartong S J 2017 *ECS J. Solid State Sci. Technol.* **6** P356

**Acknowledgments**

The Russian Science Foundation, grant № 19-19-00510 “Elaboration of a PECVD plasma-chemical method for obtaining of Gallium Oxide thin films for High-power Electronics and in Schotka Diodes” was supported this novel research. The authors are thankful to the Senior researcher of the LMCP, PhD in Chemistry, Sazanova T.S. for the AFM measuring and to the manager of the LMCP Prof. Vorotyntsev I.V. for a sensitive and attentive supervision.