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# Study of Optical and Structural Properties of β-$(Al_xGa_{1-x})_2O_3$ Thin Films Grown by Spray Pyrolysis Technique

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Abstract

The work demonstrates the synthesis of thin films of β-$(Al_xGa_{1-x})_2O_3$ by spray pyrolysis method. Temperature conditions for sol synthesis are determined to obtain thin films with a specified content of aluminum. The films are studied by scanning electron microscopy, energy-dispersive X-ray spectroscopy and optical spectroscopy. The aluminum content in the fabricated β-$(Al_xGa_{1-x})_2O_3$ films is about 3.6 at.%. The optical band gap of the films is determined as 5.0 eV.

*Keywords*: β-$(Al_xGa_{1-x})_2O_3$; Thin films; Sol-gel; Spray pyrolysis; Optical band gap

## 1. INTRODUCTION

Gallium oxide ($Ga_2O_3$) is used as a functional material for various applications due to its wide band gap (~4.8 eV) [1], high electrical breakdown field (~8 MV/cm) [2], thermal stability and radiation resistance [3–5]. $Ga_2O_3$ can form six polymorphs: α-, β-, γ-, δ-, ε-, κ-. The β phase is the most stable under normal conditions [6]. One of the directions in improving the properties of the structures based on $Ga_2O_3$ is the synthesis of the ternary $(Al_xGa_{1-x})_2O_3$ solid solutions. The $(Al_xGa_{1-x})_2O_3$ solid solutions primarily make it possible to increase the band gap in the range from 4.8 eV for β-$Ga_2O_3$ to 8.8 eV for α-$Al_2O_3$ [7–11]. In this case, the corundum α-phase is traditionally considered an insulator [12], and calculations and experiments show that for the $(Al_xGa_{1-x})_2O_3$ solid solution, the monoclinic crystal lattice of the β-phase is energetically more favorable up to 70% Al [13–15]. Therefore, the addition of Al to the β-phase of $Ga_2O_3$ is of great interest. Thin films of β-$(Al_xGa_{1-x})_2O_3$ have already been obtained previously by various methods: gas-phase epitaxy [16–18], molecular beam epitaxy [19–21], pulsed laser deposition [22], as well as the sol-gel synthesis method [23,24].

Sol-gel synthesis has been recognized as the simplest and cost-effective method for fabricating thin films of oxides. The sol-gel technique eliminates the need for expensive and complex growth equipment, special conditions for the growing atmosphere (all processes occur in air), works with available starting components (reagents) at low synthesis temperatures: maximum temperature treatment up to 1000 ºC (such conditions can be provided by a simple muffle furnace with spiral heating elements).

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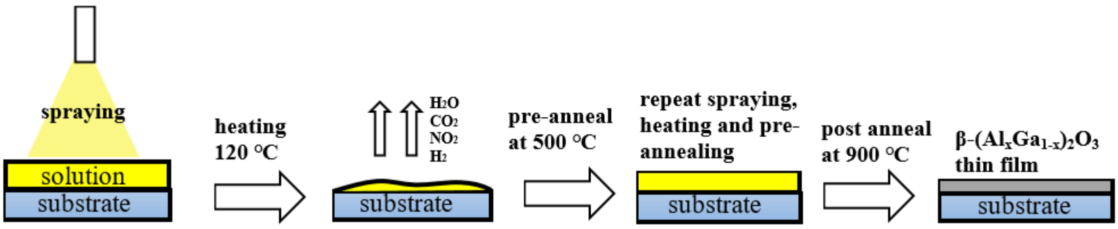


**Fig. 1.** Schematic diagram of the fabrication of β-($Al_xGa_{1-x}$)$_2O_3$ films by spray pyrolysis.

This work proposes a modification of the spray pyrolysis method for successful fabrication of β-($Al_xGa_{1-x}$)$_2O_3$ thin films. The composition and optical transmission spectra of the films are studied.

## 2. EXPERIMENT

The synthesis of β-($Al_xGa_{1-x}$)$_2O_3$ films was carried out on quartz glass ($SiO_2$) substrates. Ethylene glycol [$C_2H_6O_2$] (99.5%, Vekton, Russia) was used as a solvent; gallium nitrate [$Ga(NO_3)_3 \cdot 8H_2O$] (99.9%, Lankhit, Russia) and aluminum tri-sec-butoxide [$C_{12}H_{27}AlO_3$] (97%, Sigma-Aldrich, USA) were used as the precursors; Monoethanolamine [$C_2H_7NO$] (99.5%, Vekton, Russia) was used as a stabilizer. To obtain a sol, chemical reagents were mixed with a gradual increase in temperature from 60 to 200 °C for 1 hour.

The solution was sprayed by a high-pressure plunger pump and an outlet nozzle with a diameter of 0.1 mm. A detailed description of the installation is given in Ref. [25]. The substrate was placed on the heating table and the temperature was controlled to 120 °C. The sol was sprayed onto the substrate by pulses with a duration of 2 s. A diagram of the processes for applying a film to a substrate, including the stages of intermediate and final annealing, is shown in Fig. 1.

## 3. RESULTS AND DISCUSSION

In this work, a series of experiments was carried out on the synthesis of thin films of β-($Al_xGa_{1-x}$)$_2O_3$ using aluminum tri-sec-butoxide as the starting component of Al in an amount of 5 mol.%.

The experiments were based on a technique that was developed by the authors for the preparation of β-$Ga_2O_3$ films [25], which considered the sol-gel synthesis of gallium oxide layers, and gallium nitrate was used as the initial precursor. For this reagent, a synthesis temperature of 60 °C was sufficient for the initiation of chemical reactions. When aluminum tri-sec-butoxide is used, the synthesis temperature must be increased up to 200 °C.

When the sol heating temperature is in the range of 120–200 °C, both gallium nitrate and aluminum tri-sec-butoxide undergo gradual decomposition reactions. Amorphous aluminum oxide, gallium hydroxide and gallium oxyhydroxide particles are then formed at 200 °C. These reactions can be represented by:

$$2Ga(NO_3)_3 + 2C_{12}H_{27}AlO_3 + 22O_2\uparrow \xrightarrow{200\,^\circ C} GaO(OH) + Ga(OH)_3 + Al_2O_3 + 6NO_2\uparrow + 24CO_2\uparrow + 25H_2\uparrow. \qquad (1)$$

Figure 2 shows the sols being prepared according to the synthesis temperature. As can be seen there is a cloudy sol with partially undissolved aluminum tri-sec-butoxide at temperatures of 60–195 °C. At the temperature of 195–200 °C a transparent and homogeneous in volume sol is observed, and at 201–220 °C the sol degrades with the release water and nitride groups, which leads to yellowish color.

**Fig. 2.** Changes in the color and consistency of the sol depending on the synthesis temperature: (a) 201–220 °C, (b)195–200 °C, (c) below 195 °C.

When the sol is sprayed onto a substrate heated to 120 °C, amorphous particles of aluminum oxide, gallium hydroxide and oxyhydroxide are deposited with the removal of reaction products (organics), solvent and water. Intermediate annealing at 500 °C is required for the transition of gallium hydroxide to the amorphous phase of gallium oxide. This chemical reaction can be written as follows:

$$GaO(OH) + Ga(OH)_3 \longrightarrow Ga_2O_3 + 2H_2O. \qquad (2)$$

It can be seen from the results of the SEM image in Fig. 3 that the fabricated films have cracks. This effect may be associated with the difference in the thermal expansion coefficients of the substrate and the deposited film, as well

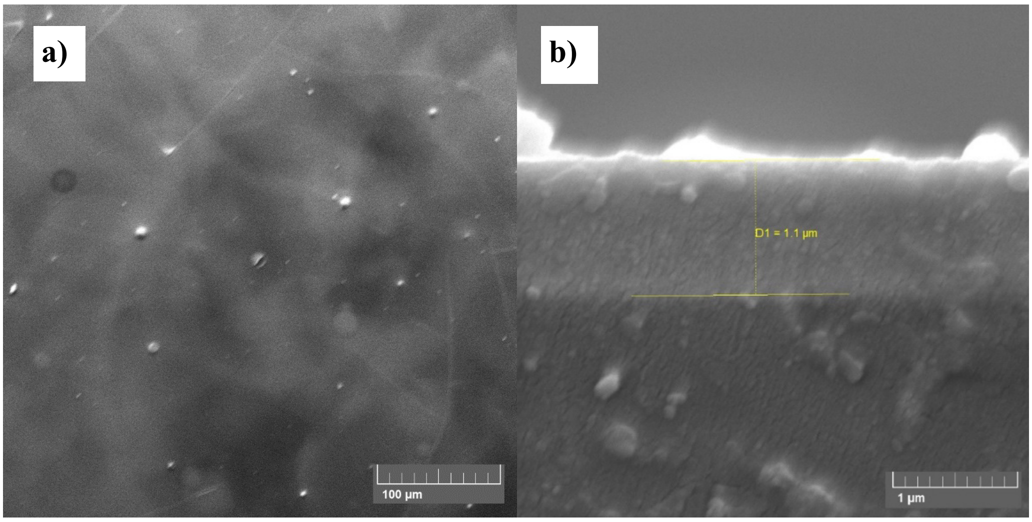


**Fig. 3.** SEM images of β-($Al_xGa_{1-x}$)$_2O_3$ films obtained by sol-gel synthesis: (a) top view of the film; (b) cross section of the film.

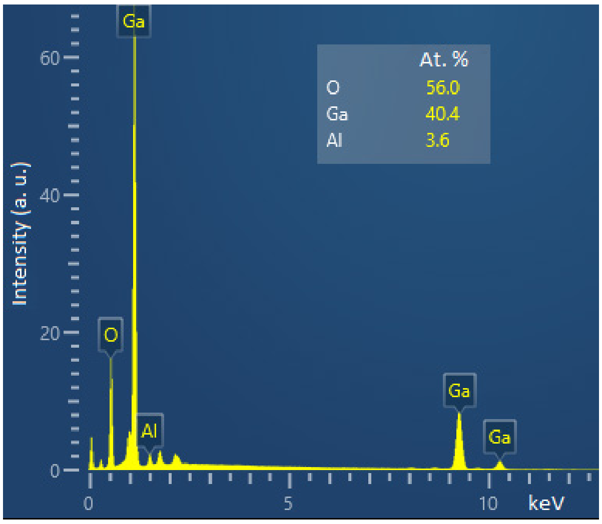


**Fig. 4.** Elemental composition of the β-($Al_xGa_{1-x}$)$_2O_3$ film analyzed by the EDS method. The mass ratio of the elements is reflected by the intensity of the peaks, while the atomic percentages shown in the inset.

as with the presence of aluminum. In our experiments, the sputtering process was repeated 30 times, and the film thickness with this number of layers was about 1 μm.

The chemical composition of the resulting films was determined by the EDS method. The results are shown in Fig. 4. The films had the correct stoichiometric composition (Ga+Al) / O = 40 / 60, uniformly distributed over the entire area with an aluminum content of about 3.6%.

The transmission spectra of the samples and the evaluation of the optical band gap are shown in Fig. 5. The samples are transparent in the near ultraviolet, visible and near infrared regions of the spectrum (wavelength from 300 to 1000 nm) and have an absorption band in the range of 200–250 nm. It can be noticed that the absorption band for samples with aluminum shifts to the UV region, which indicates the formation of the β-($Al_xGa_{1-x}$)$_2O_3$ crystal structure and an increase in the band gap compared to β-$Ga_2O_3$ films. Thus, for the β-($Al_{0.08}Ga_{0.92}$)$_2O_3$ film, the optical band gap was determined as 5 eV, see Fig. 5b.

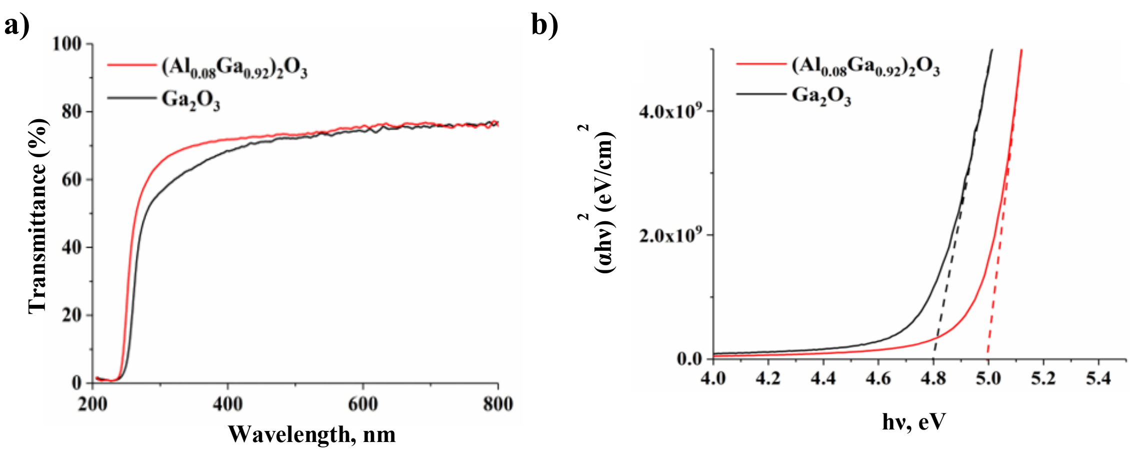


**Fig. 5.** Comparison of the optical properties of β-$Ga_2O_3$ and β-($Al_{0.08}Ga_{0.92}$)$_2O_3$ films obtained by sol-gel synthesis: (a) optical transmission spectra; (b) Tauc dependencies. The data for β-$Ga_2O_3$ are taken from Ref. [25].

## 4. CONCLUSION

We have proposed a modification of the sol-gel method (sol sputtering onto a substrate) for the preparation of thin films of β-$(Al_xGa_{1–x})_2O_3$. It has been demonstrated that a temperature of 200 °C must be used when synthesizing the sol. Analysis of the chemical composition by EDS showed the presence of Al in the resulting films with a content of about 3.6 at.%. at Al content of 5 mol.% in the starting reagents. Analysis of the transmission spectra made it possible to estimate the optical band gap of the material, which was 5.0 eV.

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УДК 539.23

# Исследование оптических и структурных свойств тонких плёнок β-($Al_xGa_{1-x}$)$_2O_3$, выращенных методом спрей-пиролиза

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**Аннотация.** В работе продемонстрирован синтез тонких пленок β-($Al_xGa_{1-x}$)$_2O_3$ методом спрей-пиролиза. Определены температурные условия синтеза золя для получения тонких пленок с заданным содержанием алюминия. Пленки исследованы с помощью сканирующей электронной микроскопии, энергодисперсионной рентгеновской спектроскопии и оптической спектроскопии. Содержание алюминия в изготовленных пленках β-($Al_xGa_{1-x}$)$_2O_3$ составляет около 3,6 ат.%. Ширина оптической запрещенной зоны материала пленок определена как 5,0 эВ.

*Ключевые слова*: β-($Al_xGa_{1-x}$)$_2O_3$; тонкие пленки; золь-гель; спрей-пиролиз; оптическая запрещенная зона