UDC 539.23

PREPARATION OF Ga_2O_3 THIN FILMS BY SPRAY PYROLYSIS

Zhang X. (ITMO University)**, D.I. Panov** (ITMO University), **V.A. Spiridonov** (ITMO University)
Scientific supervisor-Prof. A.E. Romanov (ITMO University)

Introduction. As a wide band gap semiconductor material, Ga_2O_3 is widely used in high-power semiconductor electronic devices because of its wide band gap (~4.8 eV), high breakdown electric field (> 8 MV/cm), thermal stability and radiation resistance [1]. Ga_2O_3 has six polymorphs [2,3], of which the β-phase is the most stable. We successfully prepared β-Ga_2O_3 thin films by spray pyrolysis. The spray pyrolysis method belongs to the sol-gel methods. The advantage of this method is that the equipment is simple, low cost, and uniform thin films can be obtained quickly. The chemical composition of the film was analyzed by X-ray diffraction, and it was found that the sample annealed at 900°C was β-Ga_2O_3 film. We observed the morphology of the film by scanning electron microscopy (SEM), and estimated the bandgap value of β-Ga_2O_3 to be 4.87eV by measuring the transmission coefficient of the sample.

Main part. The steps of the experiment and measurements were as follows:

1) Mix the solution and clean the substrate. Dissolve gallium nitrate [$Ga(NO_3)_3$*$8H_2O$] (99,9%) in ethylene glycol [$C_2H_6O_2$] (99.5%) and add stabilizer monoethanolamine [C_2H_7NO] (99.5%). The mixed solution was stirred at 60 °C for 1 h. The molar ratio of gallium nitrate and monoethanolamine is 3:1, and the molar concentration of gallium nitrate and ethylene glycol was 0.25 mol/l. The silica substrates were ultrasonically cleaned with isopropanol for 10 min and then dried in air.

2) Preparation of Ga_2O_3 thin films. Spray the solution onto the silica substrate using a high-pressure plunger pump with an outlet nozzle diameter of 0.1 mm. Below the substrate was a heating plate connected to a temperature controller. The distance between the substrate and the nozzle was approximately 30 cm.

The temperature of the heating plate under the substrate was 120°C, and each layer was deposited on the substrate for 2 s. The substrate was then left to dry on a hot plate for 2 min to remove carbon dioxide and water. The reaction was [4]: $Ga(NO)_3 \rightarrow GaO(OH) + Ga(OH)_3 + N_2O_5$.

After drying, the samples were pre-annealed in a muffle furnace at 500 °C for 5 min to remove organic impurities. The reaction of this process is [4]:$GaO(OH) + Ga(OH)_3 \rightarrow Ga_2O_3 + H_2O$.
The above steps were repeated until 30 thin layers were deposited. Finally, the sample was annealed at 900 °C for 2 h to convert it into β-Ga_2O_3 film.

3) Using SEM to observe the Ga_2O_3 film after annealing at 900°C. It can be seen that there are cracks in it, which may be caused by the difference in thermal expansion coefficient between the film and the silica substrate [5,6].

It can be seen from the XRD spectrum that the X-ray diffraction peak corresponds to β-Ga_2O_3.

From the transmission spectrum we can see that the sample has transmission in the near-ultraviolet, visible and near-infrared regions (300-1000 nm), and the absorption peak is in the range of 200-250 nm. After post-annealing at 900 °C, the absorption peak and transmission of the sample are enhanced. This can be explained by the transition of the film to crystalline β-phase of Ga_2O_3. After annealing at 900 °C, the bandgap value of the β-Ga_2O_3 film was estimated to be 4.87 eV by analyzing the transmission spectrum.

Conclusions. We successfully prepared β-Ga_2O_3 thin films by spray pyrolysis. We found that the transmittance and absorption peaks of the films annealed at 900°C were enhanced. This shows that the preparation of β-Ga2O3 thin films by sol-gel method has the advantages of high efficiency, low cost, and easy to obtain uniform thin films, and has broad development prospects.

Reference:

1. Stepanov S.I., Nikolaev V.I., Bougrov V.E., and Romanov A.E. Gallium OXIDE: Properties and applications - a review // Rev. Adv. Mater. Sci. – 2016. – № 44. – P. 63–86.
2. Roy R., Hill V.G., Osborn E.F. Polymorphism of Ga_2O_3 and the System Ga_2O_3 - H_2O // Journal of the American Chemical Society. – 1952. – Vol. 74, № 3. – P. 719–722.
3. Playford H.Y., Hannon A.C., Barney E.R., Walton R.I. Structures of Uncharacterised Polymorphs of Gallium Oxide from Total Neutron Diffraction // Chemistry – A European Journal. – 2013. – Vol. 19, № 8. P. 2803–2813.
4. Berbenni V., Milanese C., Bruni G., Marini A. Thermal decomposition of gallium nitrate hydrate $Ga(NO_3)_3 \times xH_2O$ // Journal of Thermal Analysis and Calorimetry. – 2005. – Vol. 82, – № 2. – P. 401–407.
5. Víllora E.G., Shimamura K., Ujiie T., Aoki K. Electrical conductivity and lattice expansion of β-Ga_2O_3 below room temperature // Applied Physics Letters. – 2008. – Vol. 92, – № 20. – P. 202118.
6. Oishi J., Kimura T., Thermal Expansion of Fused Quartz. . // Metrologia. –1969. – Vol. 5, № 2. – P. 50–55.