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Study of Ga_2O_3 deposition by MOVPE from trimethylgallium and oxygen in a wide temperature range

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Study of Ga_2O_3 deposition by MOVPE using trimethylgallium and oxygen was performed in a wide temperature range. It was found that for Ga_2O_3 deposition rate vs temperature dependence is very close to the TMGa pyrolysis in nitrogen. Kinetically-limited range for these processes corresponds to 550−700°C, that is 150°C higher, then for GaN deposition in the same reactor.

Keywords: gallium oxide, MOVPE

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Gallium oxide Ga_2O_3 is a promising material for semiconductor electronics. Its properties and synthesis technology have been studied extensively in recent years [1,2]. Unfortunately, the studies of its epitaxial growth are focused on a narrow range of optimum conditions. Specifically, no data on the influence of temperature varying within a wide interval on the deposition rate have been published. These data are needed in order to gain a thorough understanding of the mechanism of metalorganic vapor-phase epitaxy (MOVPE) with due account for chemical and physical processes within the entire reactor volume and to optimize the geometry of epitaxial reactors. In the present study, the dependence of the Ga_2O_3 deposition rate in MOVPE on temperature varying within a wide interval is examined. The obtained results are compared to the well-known dependences for GaN and metallic gallium (individual pyrolysis of trimethylgallium). In order to exclude the influence of the reactor design and the temperature measurement method on the results, we measured these dependences directly in the same reactor under similar conditions.

Just as in any other chemical vapor-phase epitaxy process, the temperature dependence of the deposition rate in MOVPE features three well-marked sections. At low temperatures, the deposition rate is governed by the rate of surface chemical reactions. This growth regime is called a kinetically limited one. In the simplest case, a linear section of the Arrhenius curve corresponds to it. The kinetic section is shifted toward lower (compared to the dependence for individual pyrolysis of a metalorganic compound) temperatures in the presence of molecular and, even more so, atomic hydrogen, which may be supplied by group V hydrides. At higher temperatures, the deposition rate is governed by the transport of components to the surface (i.e., the rate of diffusion through the boundary layer). The temperature dependence is weak. As the temperature increases further, the deposition rate decreases due to the material decomposition, depletion of the vapor phase, or parasitic reactions.

Trimethylgallium (TMGa) ignites spontaneously in air under normal conditions. The concentration of oxygen in the reactor atmosphere in our experiments was 5−30 mol.%. This level is comparable to the concentration of oxygen in air. The extremely low concentration of TMGa vapor ($\sim 2 \cdot 10^{-4}$) made feasible the prospect that combustion would not occur. However, the oxidation reaction was expected to proceed at fairly low temperatures. The actual process was quite unlike the predicted one.

Experiments were performed using an Epiquip-VP 50 RP setup upgraded for growth of group III oxides (with the growth of their nitrides still being supported). TMGa, ammonia (NH_3), and oxygen (O_2) were used as precursors. The setup features a horizontal reactor with induction heating. The internal reactor is connected to an injector with two slot nozzles. O_2 is fed into the reactor through one of these nozzles in the process of oxide growth, and a mixture of metalorganic vapor and a carrier gas is fed through the other nozzle. When nitrides are being grown, NH_3 is also fed through it. Nitrogen and argon were used as carrier gases in deposition of Ga_2O_3 (no difference was observed; the majority of experiments were performed in nitrogen), and nitrogen and hydrogen were used to deposit GaN and metallic gallium. All materials were deposited onto sapphire (0001) substrates.

The conditions in the reactor in deposition of GaN, metallic gallium, and Ga_2O_3 differed slightly. The TMGa flow in deposition of all materials was 49 μmol/min (unless indicated otherwise). GaN and metallic gallium were deposited under a pressure of 200 mbar and with a total gas flow of ~ 8 slm (standard liter per minute). The flow of NH_3 in GaN growth was 3 slm. These conditions are the optimum ones for GaN growth in the given reactor. The deposition of Ga_2O_3 was performed under a pressure of 100 mbar and with a total gas flow of 5 slm. Unless indicated otherwise, the flow of O_2 was 0.5 slm. These conditions were identified as the tentatively optimum ones for epitaxial Ga_2O_3 growth in the given reactor. It is clear that the comparison would be more correct if the process conditions were the same. On the other hand, different materials require different growth conditions. We plan to conduct a more thorough investigation in overlapping ranges of process parameters in the future.

The results of the above experiments were compared to the ones obtained in a vertical reactor with triethylgallium (TEGa) and O_2 used as precursors. The pressure in the reactor was 80 mbar, the total gas flow was 1.4 slm, argon was the carrier gas, the oxygen flow was 0.4 slm, and the TEGa flow was 25 μmol/min.

The deposition rates of Ga_2O_3 and GaN were measured by laser reflectometry. The deposition rate of Ga was determined by weighing the substrate before and after the process.

Figure 1 shows the temperature dependences of the deposition rate of Ga_2O_3, GaN, and metallic gallium. The effects mentioned above are seen clearly: the kinetic section in GaN deposition corresponds to the 450–550°C temperature interval (naturally, the lower boundary is tentative), which is the same for both types of carrier gas. In the case of individual pyrolysis of TMGa in nitrogen atmosphere, this section is located at substantially higher temperatures (600–700°C). When nitrogen is substituted with hydrogen, the characteristic pyrolysis temperature decreases by 60–70°C (not shown in the figure). It was unexpected that the deposition of Ga_2O_3 proceeded at fairly high temperatures. The major part of the dependence almost matches the dependence for TMGa pyrolysis in nitrogen. The only difference is in the low-temperature part, where Ga_2O_3 is deposited very slowly (although much faster than metallic gallium). Thus, contrary to our expectations, oxygen activates the process of TMGa decomposition only slightly. At the same time, the growth rate remains high even at 550°C if TEGa is used as a precursor. The rate even decreases at higher temperatures (possibly, due to additional losses in the vertical reactor). The growth rate in this series of experiments (TEGa, vertical reactor) is, in general, ~ 2 times lower than the one corresponding to the diffusion section in experiments with TMGa and the horizontal reactor, although the concentration of the group III precursor is approximately 2 times higher. The nature of this difference requires further investigation.

Figure 2, *a* shows the dependences of the deposition rate of Ga_2O_3 on the flow of oxygen at two different temperatures. It is evident that the above assumption of the lack of activation of the TMGa decomposition by oxygen is not entirely correct. The flow of oxygen does not affect the deposition rate in the diffusion-limited section (775°C), while an increase in the flow of oxygen in the kinetic section (710°C) translates into an increased deposition rate, although the dependence is substantially sublinear.

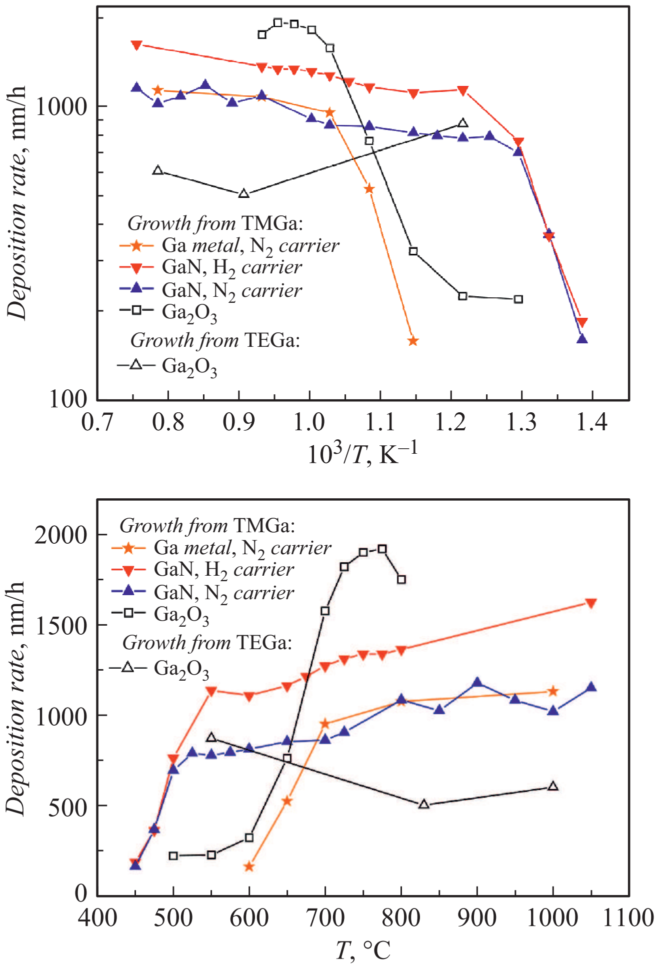

Figure 1. Temperature dependences of the deposition rate of Ga_2O_3, GaN, and metallic gallium plotted in different coordinates.

At the end of this preliminary study, the dependences of the deposition rate of Ga_2O_3 on the TMGa flow were measured at different temperatures. Although a certain sublinearity is seen in Fig. 2, *b* in the temperature range corresponding to the hot half of the kinetic section, the dependences are generally close to linear ones.

Numerical simulations of the process of deposition of Ga_2O_3 films and metallic gallium in nitrogen with account for flow, heat transfer, mass transfer, and processes in the vapor phase and on the growth surface were performed to reveal the mechanisms of growth.

It is assumed that the vapor phase has the following components:

— precursors: TMGa, O_2 (molecular oxygen);

— carrier gas: N_2 (nitrogen);

— products of decomposition of precursors: MMGa (monomethylgallium), as well as $DMGaOCH_3$ (dimethylgallium monomethoxide) and $[DMGaOCH_3]_2$ (dimer of dimethylgallium methoxide) that are produced in reactions of TMGa with oxygen [3–5]; CH_3 may react and produce ethane (C_2H_6), and reactions with oxygen, which may proceed at the studied temperatures, were also considered [6].

Surface reactions include the adsorption of metallic gallium and CH_3 radicals from TMGa onto vacant Ga sites on the surface and the adsorption of oxygen onto vacant oxygen sites. The desorption of CH_3 from the surface (the corresponding reaction activation energy is 41 kcal/mol [7]) and reactions of formation of metallic gallium and gallium oxide from surface components are taken into account in the model.

Figure 3 presents the comparison between the results of numerical simulation and the experimental dependences. According to the model, the deposition rate of materials in the kinetic growth regime (600–670°C) is limited by the blocking of vacant sites for gallium adsorption by CH_3 radicals. The growth rates for Ga and Ga_2O_3 should be the same regardless of the fact that the molar fraction of TMGa at the reactor inlet is ~ 1.7 times higher in the case of growth of gallium oxide. This effect is weakened at high temperatures ($T > 675°C$) by the enhancement of desorption of CH_3, and the growth rate is governed by the transport of TMGa to the surface. It can be seen that the results of simulation of Ga deposition agree closely with the experimental data in the 600–1000°C range, but the growth rate of Ga_2O_3 at temperature $T > 725°C$ was slightly below the transport limit. The reduction in the deposition rate is attributable to the formation of heavy components $[DMGaOCH_3]_2$ in the vapor phase, and calculated data confirm this. The rate of deposition from such components is lower than the rate of growth from TMGa, since the diffusion coefficients of components in the gas phase are lower. The effect of parasitic reactions is the most probable cause of moderation of growth at $T = 800°C$: according to preliminary estimates, the rate of etching of Ga_2O_3 by hydrogen produced in the chain of reactions of CH_3 with oxygen is too low due to the low concentration of CH_3. The model reproduces quantitatively the variation of the crystal deposition rate with TMGa flow. The model evidently needs to be refined, since it underestimates slightly the deposition rate at a temperature of $\sim 650°C$, and the deposition rates predicted by it at low ($< 600°C$) temperatures differ noticeably from the experimental values.

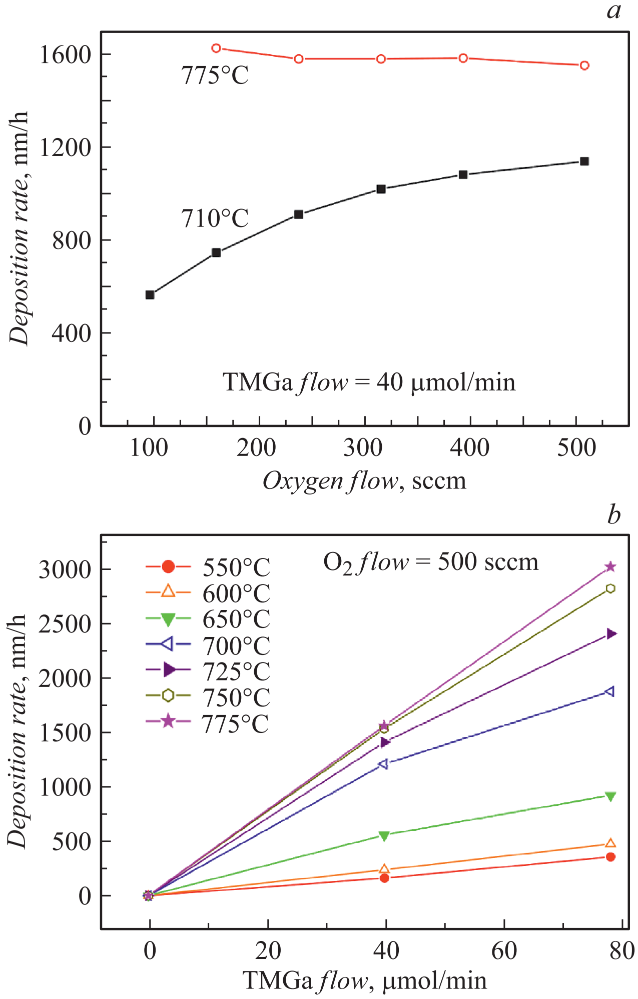

Figure 2. Dependences of the deposition rate of Ga_2O_3 on the flow of oxygen (*a*) and TMGa (*b*) at different temperatures.

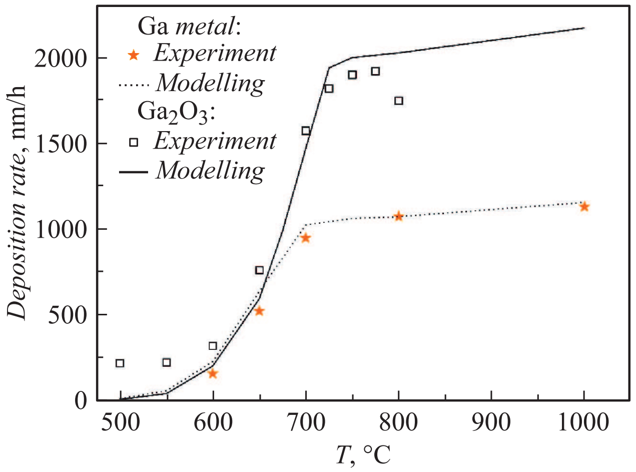

Figure 3. Comparison between the temperature dependences of experimental (symbols) and calculated (curves) deposition rates of metallic gallium and Ga_2O_3 (nitrogen is the carrier gas).

Thus, the temperature dependence of the Ga_2O_3 deposition rate was examined. The proposed model of deposition provides a close fit to the experimental data in the diffusion section and the major part of the kinetic section of the dependence.

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Conflict of interest

The authors declare that they have no conflict of interest.

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