Study of Ga$_2$O$_3$ deposition by MOCVD

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Abstract. Growth of Ga$_2$O$_3$ by metalorganic chemical vapour deposition in horizontal flow reactor from trimethylgallium (TMG) and oxygen is studied in a wide temperature range. The growth rate is directly proportional to TMG flow, weakly affected by O$_2$ flow and non-monotonically depends on temperature. Growth rate over 3 $\mu$m/h is demonstrated, indicating that TMG can be used for growth of $\beta$-Ga$_2$O$_3$ thick layers for device applications.

1. Introduction
The development of semiconductor electronics requires extension of material systems used. Last decade a lot of attention is paid to III-oxides, because of its unique properties: wide band gap (4.9 eV for Ga$_2$O$_3$ [1]), high breakdown voltage (expected to be over 6 MV/cm [2]). The drawbacks are indirect bandgap, problem with p-type doping and low thermal conductivity (10-30 W/mK, that is 10 times lower than for GaN) [3]. Based on these properties, III-oxides have attracted much attention for its application potential in power high-voltage devices [4] and UV photodetectors.

Many results published were obtained using triethylgallium (TEG) as source of Ga. Thick epitaxial layers are needed for high voltage power devices and deep ultraviolet solar-blind photodetectors, but growth rate from TEG is somehow limited be its lower vapor pressure, TMG is most widely used metalorganic gallium precursor, and its cheaper than TEG.

In this paper, we present the study of the influence of the epitaxy conditions on Ga$_2$O$_3$ growth rate for horizontal flow MOCVD system.

2. Experimental
Samples were grown by metal-organic chemical vapor deposition (MOCVD) on (0001) sapphire substrates or AlN/Si(111) templates in a specially designed horizontal flow reactor with inductively heated susceptor. MOCVD system has a capacity of one 2 inch substrate and designed to perform epitaxy of nitride and oxide materials in a one reactor. Trimethylgallium (TMG) and oxygen were used as precursors, and nitrogen or argon were used as carrier gas. TMG flow was varied up to 96 $\mu$mol/min and O$_2$ flow was varied from 100 to 500 sccm. Carrier gas flow and reactor pressure was kept constant at 4 slm and 100 mbar, respectively, in a whole set of experiments for both gases used. No buffer layer was used. Growth rate and surface roughness during epitaxy was controlled by in-situ reflectometry system operating at 633 nm.
Samples were characterized by X-ray diffraction using powder diffractometer D2 Phaser. Raman spectra of the studied samples were measured at room temperature in backscattering geometry using a T64000 spectrometer (Horiba Jobin-Yvon, France) equipped with a confocal microscope and a silicon CCD cooled by liquid nitrogen. The line at $\lambda = 532$ nm (2.33 eV) of Nd:YAG laser (Torus, Laser Quantum, Inc., UK) was used as the excitation source.

3. Results and discussion

At a first stage a set of epitaxial runs were done at various growth conditions to establish range of temperatures suitable for Ga$_2$O$_3$ deposition. Figure 1 presents dependences of growth rate (GRR) on temperature for two TMG flows using N$_2$ carrier gas and effect of carrier gas change to Ar at maximal TMG flow. In a dependence of growth rate on temperature two regions can be separated: at lower temperatures below ~725°C growth rate is strongly affected by temperature (kinetically-limited regime) and strong influence of carrier gas is observed; at higher temperatures we have diffusion-limited growth. For temperatures above 750°C growth rates saturates and drop. GRR dependencies for growth on AlN/Si templates are the same as for growth on sapphire, but a bit shifted to lower temperatures, indicating more effective heating of silicon substrate. To check the nature of GRR drop at several temperatures we perform growth at various TMG flows. GRR is strictly proportional (within experiment accuracy) to TMG flow for all temperatures studied without any tendency for saturation, indicating that there are no parasitic reactions in a gas phase, and observed effect is possibly due to depletion of TMG caused by deposition on hot part of susceptor. GRR vs temperature dependence significantly differs from reported in [5] simulation and experimental results from [6], but this can be explained by principal difference in reactor design.

![Figure 1. Dependences of growth rate on temperature for various TMG flows and carrier gases.](image1)

![Figure 2. Dependence of growth rate on oxygen flow for various temperatures.](image2)

Dependence of GRR on oxygen flow is presented on fig.2. At 775°C GRR is nearly independent on O$_2$ flow, and at lower temperature of 710°C weak dependence can be observed. For this set of experiments VI/III ratio was varied from 90 to 450, and we have found that sample optical and structural quality strongly depends on it, for high VI/III ratio samples were transparent, but for lower ratios became of greyish colour and even become amorphous, so we decrease TMG flow further and next sample was grown with the following growth conditions: growth temperature 750°C, TMG flow 32 µmol/min, O$_2$ flow 500 sccm and N$_2$ carrier gas. Film thickness was ~2700 nm.

Fig. 3 shows the X-ray diffraction curve of the sample. The diffraction peaks indicate that the film is polycrystalline $\beta$-Ga$_2$O$_3$ material with domination of (-201)-oriented phase as typical for growth on sapphire [8]. No other polytypes were revealed. The film is highly resistive so we could not perform Hall measurements on it, what may be due to carbon incorporation [7].
Figure 3. Diffraction curve of Ga$_2$O$_3$ epilayer grown on sapphire. Al$_2$O$_3$ (006) reflection is marked by asterisk.

Figure 4 shows the typical Raman spectrum of Ga$_2$O$_3$ film grown on Al$_2$O$_3$ (0001) substrate and the spectrum of a bulk $\beta$-Ga$_2$O$_3$ crystal. Under ambient growth conditions, the stable form of Ga$_2$O$_3$ is monoclinic ($\beta$-Ga$_2$O$_3$), which belongs to the space group C2/m. The primitive cell of $\beta$-Ga$_2$O$_3$ contains 10 atoms. As a result, there are 3 acoustic and 27 optical phonons in the vibrational spectrum of this crystal. According to the selection rules, 10 modes of $A_g$ symmetry and 5 modes of $B_g$ symmetry should be observed in the first-order Raman spectrum of the $\beta$-Ga$_2$O$_3$ crystal [9, 10].

Figure 4. Unpolarized Raman spectra of Ga$_2$O$_3$/Al$_2$O$_3$ film (1) and a bulk $\beta$-Ga$_2$O$_3$ crystal (2), measured in the backscattering geometry $\mathbf{z}(\mathbf{x}+\mathbf{y})\mathbf{z}$. Here, the $z$ axis is the direction perpendicular to the sample plane, and $x$ and $y$ axes are oriented in the plane. The inset shows the Raman spectra in the region of the $A_{1g}^{(3)}$ phonon.

Comparison of the Raman spectra of the Ga$_2$O$_3$/Al$_2$O$_3$(0001) film, the bulk $\beta$-Ga$_2$O$_3$ crystal, and the data from [9] revealed the presence in the spectrum of the Ga$_2$O$_3$/Al$_2$O$_3$(0001) film of all allowed
phonon modes, which are characteristic of the monoclinic $\beta$-Ga$_2$O$_3$ system. Thus, it can be concluded that the grown film has the $\beta$-Ga$_2$O$_3$ structure. The analysis of the Raman spectra shown in figure 4 revealed that the position of all lines practically coincides. As an example the most intense phonon line $A_{2g}^{(3)}$ of the grown Ga$_2$O$_3$/Al$_2$O$_3$(0001) film and phonon line $A_{2g}^{(3)}$ of bulk $\beta$-Ga$_2$O$_3$ are shown in the inset in figure 4. This fact allows us to conclude that there is no strain in the grown $\beta$-Ga$_2$O$_3$ film. However, comparison of the phonon line width at half maximum (FWHM) (see inset in figure 4) of the Ga$_2$O$_3$/Al$_2$O$_3$(0001) layer (FWHM=3.2 cm$^{-1}$) and bulk $\beta$-Ga$_2$O$_3$ crystal (FWHM=2.3 cm$^{-1}$) leads to conclusion that the structural quality of the epitaxial $\beta$-Ga$_2$O$_3$ film is somewhat worse than that of the bulk $\beta$-Ga$_2$O$_3$ crystal.

4. Conclusion
In summary, $\beta$-Ga$_2$O$_3$ thin films were grown by MOCVD using trimethylgallium as a source for gallium and pure oxygen for oxidation. It was revealed that growth rate of the films strongly depends on temperature and proportional to TMG flow, and quality of film is governed by VI/III ratio. The results presented here demonstrate the suitability of the TMG source for the MOCVD growth of $\beta$-Ga$_2$O$_3$ films at horizontal flow reactors with fast growth rate, which is required for practical use.

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