

Characterization of Crystalline Structure and Morphology of Ga₂O₃ Thin Film Grown by MOCVD Technique

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Abstract. Growth of gallium oxide thin film was realized with MOCVD on (0001) sapphire substrate. Structural and compositional properties of thin film were studied employing trimethylgallium and water as precursors, carrier gases were H₂ and N₂. Obtained film is polycrystalline and predominantly consisted of (201) oriented β-Ga₂O₃. Sample exhibited blue luminescence which is attributed to oxygen vacancies. H₂ gas proved to have beneficial effect on film quality and overall growth process.

Introduction

Gallium oxide (Ga₂O₃) is wide band gap (~5 eV) transparent semiconducting oxide (TSO), therefore it could be assessed as candidate for power electronics (high voltage FET) [1] and optoelectronics (deep ultraviolet photodetectors) [2] applications, as well as template material for others semiconducting materials [3]. Potential of Ga₂O₃ is known for decades, but profound interest from industry side was not observed until recent events. Reasons hold semiconductor industry itself, as semiconductor applications set much higher standards for material quality, purity and cost-effectiveness than conventional manufacturing methods could provide. Ga₂O₃ bulk crystal growth is inherently hard and undesired because of the incongruent melting at high temperature (1820° C), high free carrier absorption in the near infrared wavelength range and strong cleavage planes [4]. All this leads to high process expenses, poor crystal quality and purity. Logical alternative is to use recently established method in semiconductors industry – metal organic chemical vapor deposition (MOCVD). This heteroepitaxial method allows obtaining high quality thin films like GaN, SiC, etc. on sapphire substrate. In this research paper crystal structure and quality of Ga₂O₃ thin film deposited on sapphire by MOCVD was investigated.

Experimental methods

The hetero epitaxial Ga₂O₃ thin film was grown on a c-plane sapphire substrate using commercial AIXTRON (AIX-200RF) MOCVD system. Trimethylgallium (TMG) and water was employed as precursors. Before growth, sapphire wafer was annealed for two minutes at 1200 C in hydrogen flow. Precursor carrier gases were hydrogen and nitrogen. Total flow through reactor was 2700 sccm. The TMG and water were stored in stainless steel containers with thermostat stabilized temperature 5 °C for TMG and 20°C for water. Reactants were transported into the reactor with a flow rate of 20 sccm and 500 sccm at atmosphere pressure respectively, corresponding calculated molar concentrations are 0.118 mmol/min for TMG and 0.513 mmol/min for water. The growth pressure was kept at 15 mBar and the substrate temperature was 820° C. Obtained film thickness is 1.3 micrometers (Fig. 4.), measured growth rate was 650 nm/h.

For photoluminescence (PL) measurements a grating monochromator MCD was used for registration of luminescence spectra and BM-2 for luminescence excitation spectra (PLE). Light source was deuterium discharge L10366 Hamamatsu. Luminescence detection was done with H8259-01 photon counting module Hamamatsu. Sample was held on finger of cryostat. Liquid nitrogen was used for cooling. PLE spectrum was determined as luminescence intensity at different

excitation energies devised on light falling on the sample. Sodium salicylate was used in both cases as light transformer for determination of excitation light intensity.

Structural properties of the film were determined by X – ray diffraction (XRD, PANalytical X'Pert Pro MPD diffractometer, equipped with multichannel detector PIXcel, Cu radiation with $U = 45$ kV, $I = 40$ mA). PDF-2 and COD [5] databases were used for XRD peaks identification.

For the imaging atomic force microscope (AFM) Veeco CP II has been utilized. The scanning was performed using silicone probes with typical tip radius < 10 nm in tapping regime. The scan rate was kept between 0.3-0.5 Hz.

Results and discussion

Fig. 1 shows luminescence and excitation spectra of β - Ga_2O_3 at 180K. PL of studied sample is absent at 293 K. PL could be observed below 200 K. Practically one PL band at about 3 eV and a series of excitation bands are obtained. The quality of the sample does not allow unequivocally determine intrinsic absorption threshold; however it is higher than 4 eV, because luminescence spectrum is ranging up to 4.2 eV. After excitation spectra it is possible to estimate the absorption threshold around 4.6 eV, which corresponds to Ga_2O_3 band gap. PL measurements show clear blue emission band (3 eV). This indicates that oxygen vacancies, presumably responsible for the n-type conductivity [6], are involved in the blue emission process. Blue emission originates from the recombination of an electron on a donor and a hole on an acceptor. Possible donors are V_O and Ga_i , and possible acceptors are V_Ga and/or the V_O - V_Ga complex [7]. It is expected that the present growth conditions would easily produce considerable quantity of oxygen vacancies and gallium–oxygen vacancy pairs due to high temperature and oxygen-deficient ambient.

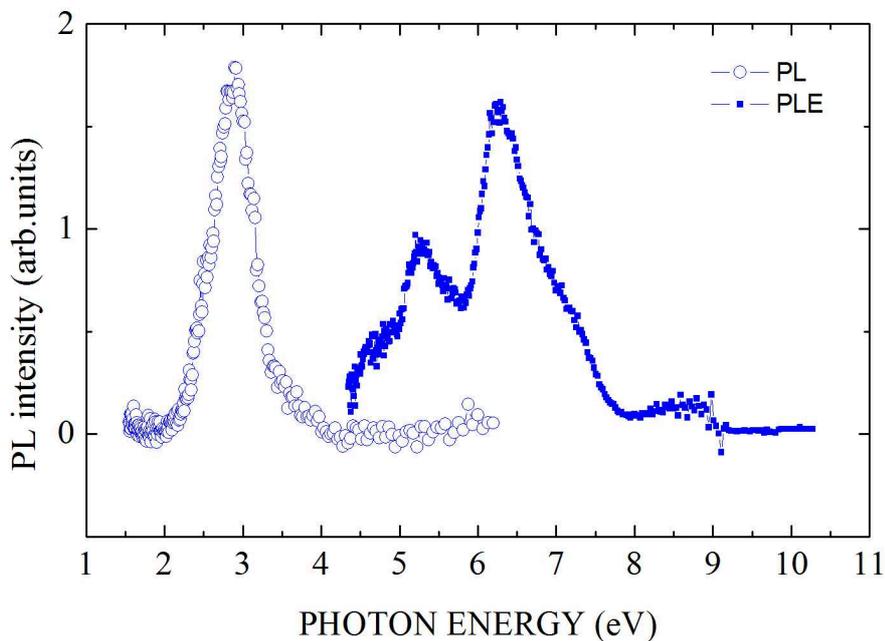


Fig. 1. Luminescence and excitation spectra of β - Ga_2O_3 at 180K.

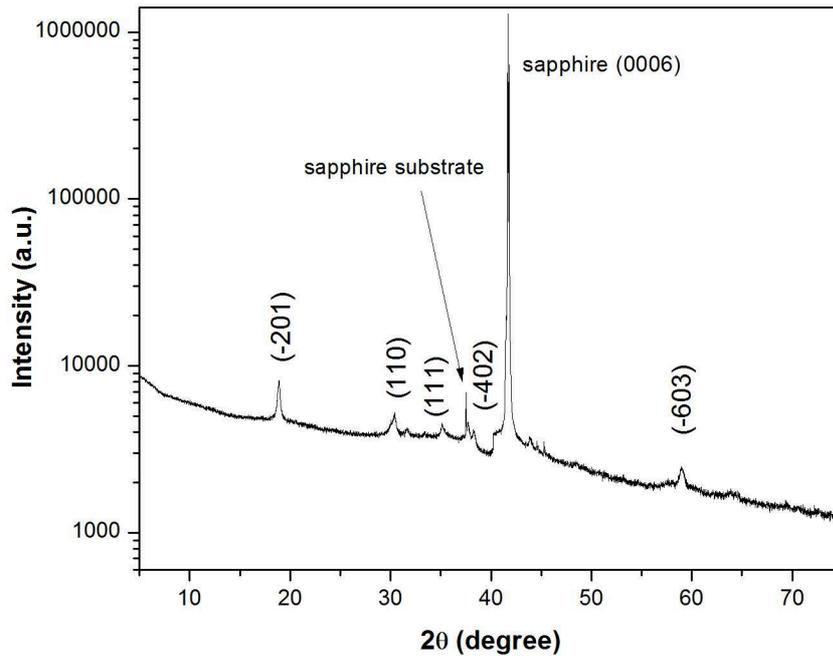


Fig. 2. XRD 2θ scans of β - Ga_2O_3 thin film deposited on (0001) sapphire substrate.

Fig. 2. depicts XRD patterns of Ga_2O_3 films crystallized during deposition on sapphire C-planes under flowing H_2 gas. Diffraction peaks of $(\bar{2}01)$, $(\bar{4}02)$, $(\bar{6}03)$ appeared at 19, 38 and 59 degrees. Peak at 37.5 degrees originate from sapphire substrate. These $(\bar{2}01)$ series peaks appearing with comparable intensities are characteristic of β - Ga_2O_3 , as has been reported in the literature [8-10]. β - Ga_2O_3 has a monoclinic structure and belongs to the $C2h$ space group. Obtained film mainly consists of $(\bar{2}01)$ β - Ga_2O_3 , however because other orientation diffraction peaks has been identified as β (110) at 30 degrees and β (111) at 35 degrees, film is not mono crystalline. Reason for predominant $(\bar{2}01)$ oriented Ga_2O_3 growth is due to the oxygen atoms in the $(\bar{2}01)$ equivalent plane of β - Ga_2O_3 have the same arrangement as the oxygen atoms of the Al_2O_3 (0001) plane. While the corresponding XRD patterns in Fig. 2 have diffraction peaks that belong to β - Ga_2O_3 , their peak intensities are approximately one third of $(\bar{2}01)$ peak intensity, which indicate appreciable volume of misoriented domains.

Although film is polycrystalline, obtained film has descent quality, compared with previous results using water as oxygen source. AFM investigation shows specific surface structure features with overall roughness around 10 nm, this indicates inclusions of misoriented domains along [110] and [111] axes. Roughness for high quality films should be below 1 nm [11].

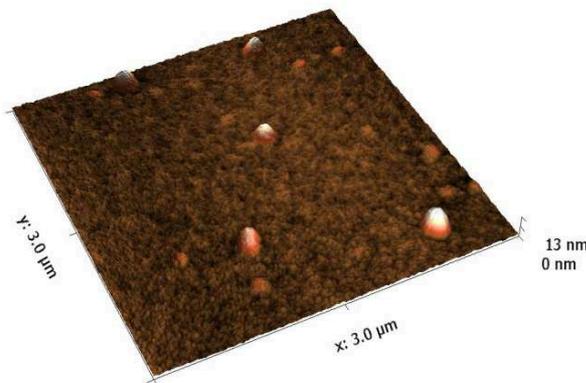


Fig. 3. AFM image of β - Ga_2O_3 thin film surface morphology.

Using hydrogen as carrier along nitrogen promoted better film growth and improved film quality substantially. Previously, for Ga_2O_3 film growth we used only nitrogen as carrier gas, but these films had poor quality, we unable to measure surface with AFM. We rationalized that hydrogen promotes stoichiometric film growth, by increasing gallium desorption from growth interface.

Although presence of reducing atmosphere (H_2) may inhibit oxygen incorporation in crystal lattice as PL measurements indicates. SEM depicts smooth surface layer of Ga_2O_3 (light) on sapphire substrate (dark).

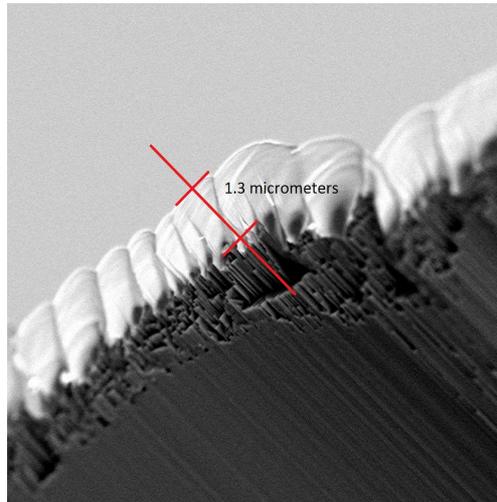


Fig. 4. SEM image of β - Ga_2O_3 thin film on sapphire substrate; 5600x; 10 kV image.

Summary

The β - Ga_2O_3 film was deposited on sapphire (0001) substrates by MOCVD using trimethylgallium as gallium source and water as oxygen source. Hydrogen along nitrogen was used as carrier gas. Structural and compositional properties of the films were investigated in detail. Photoluminescence measurements showed pronounced blue emission around 3 eV, which indicated presence of oxygen vacancies. Excitation spectra revealed intrinsic absorption threshold around 4.7 eV. XRD characterization revealed that the grown film was preferentially oriented along $[\bar{2}01]$, but presence of undesired auxiliary peaks indicated that film was not monocrystalline. AFM measurements showed surface roughness below 10 nm, indicating slightly misoriented epitaxial growth mechanism.

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