



Study on β-Ga₂O₃ Films Grown with Various VI/III Ratios by MOCVD

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Abstract: β -Ga₂O₃ films were grown on sapphire (0001) substrates with various O/Ga (VI/III) ratios by metal organic chemical vapor deposition. The effects of VI/III ratio on growth rate, structural, morphological, and Raman properties of the films were systematically studied. By varying the VI/III ratio, the crystalline quality obviously changed. By decreasing the VI/III ratio from 66.9×10^3 to 11.2×10^3 , the crystalline quality improved gradually, which was attributed to low nuclei density in the initial stage. However, crystalline quality degraded with further decrease of the VI/III ratio, which was attributed to excessive nucleation rate.

Keywords: β-Ga₂O₃; MOCVD; VI/III ratio

1. Introduction

 β -Ga₂O₃, the most stable phase of Ga₂O₃, shows great potential because of its excellent material properties. It is a wide bandgap (WBG) semiconductor with band gap of ~4.9 eV, breakdown field of 8 MV cm⁻¹ and Baliga's figure of merit of 3444 at room temperature, which offers more advantages in high-efficiency power device application than SiC and GaN [1]. Moreover, its high transparency in UV wavelength range, and excellent thermal and chemical stability also have great application potential in flat panel displays, UV detectors, and high-temperature gas sensors [2–6]. There are several ways to produce a β -Ga₂O₃ film, which include molecule beam epilayer (MBE) [7], metal organic chemical vapor deposition (MOCVD) [8], halide vapor phase epitaxy (HVPE) [4], chemical vapor deposition (CVD) [9], magnetron sputtering [10], and thermal oxidation [11]. Conventional CVD methods [12–14], especially MOCVD have several advantages, including excellent reproducibility and capability for scale-up to high-volume production [15]. Impressive studies on the growth of β -Ga₂O₃ by MOCVD have been recently reported. Ly et al. investigated the epitaxial relationship between β -Ga₂O₃ and sapphire substrates [16]. Zhuo et al. studied the control of the crystal phase composition of the Ga_2O_3 thin film [17]. Sbrockeyet al. demonstrated the large-area growth of β -Ga₂O₃ films using rotating disc MOCVD reactor technology [15]. Alema et al. studied the growth rates of β -Ga₂O₃ epitaxial films by close coupled showerhead MOCVD [18]. Takiguchi et al. studied β -Ga₂O₃ epitaxial films obtained by low temperature MOCVD [19]. Chen et al. investigated the effect of growth pressure on the characteristics of β -Ga₂O₃ films grown on GaAs (100) substrates [20]. However, the crystalline quality of heteroepitaxial β -Ga₂O₃ films has not been able to meet the requirements of device fabrication so far.

In this paper, β -Ga₂O₃ films were grown by MOCVD on sapphire (0001) substrates with various VI/III ratios. In addition, the effects of VI/III ratio on growth rate, structural, morphological, and Raman



properties were systematically studied. By varying the ratio, the crystalline quality of the films was effectively improved.

2. Materials and Methods

2.1. Materials

High purity O₂ (purity, 5 N) and trimethylgallium (TMGa, 6 N in purity, Nata Opto-electronic Material Co., Nanjing, China) and were used as oxidant and organometallic source, respectively. High purity Ar (purity, 6 N) worked as a carrier gas.

2.2. Preparation

The β -Ga₂O₃ films were grown on sapphire (0001) substrates by MOCVD. The equipment was modified from an Emcore D180 MOCVD (Emcore, Alhambra, CA, USA). The close coupled showerhead method is used; the highest growth temperature of the MOCVD was 1150 °C. Before the growth process, the substrates were cleaned sequentially by acetone, ethanol, deionized water in an ultrasonic bath, and then dried with N₂. The growth pressure and substrate temperature were kept at 20 mbar and 750 °C during the whole growth process, respectively. High purity O₂ was injected into the reaction chamber with a fixed flow rate of 1200 sccm. TMGa was stored in a stainless steel bubbler, maintained at 1 °C. The pressure inside the bubbler were kept at 900 Torr. Ar carrier gas passed through the TMGa bubbler and delivered the TMGa vapor to the reactor. To obtain β -Ga₂O₃ films grown with various VI/III ratios, the flow rates of Ar carrier gas were varied from 5 sccm to 60 sccm (5 sccm, 15 sccm, 30 sccm, 45 sccm, 60 sccm). The growth time was 30 min.

2.3. Characterization

The structural properties of β -Ga₂O₃ films were investigated by X-ray diffractometer (XRD, Rigaku, Ultima IV, Tokyo, Japan, $\lambda = 0.15406$ nm, graphite filter). The morphological properties of the β -Ga₂O₃ films were studied by field emission scanning electron microscopy (FESEM, JSM-7610F, JEOL, Tokyo, Japan) and atomic force microscopy (AFM, Veeco, Plainview, NY, USA). Raman properties of the films was analyzed by a Raman spectrometer (HORIBA, LABRAM HR EVO, Kyoto, Japan) using a wavelength of $\lambda = 633$ nm laser. The thicknesses of the films were measured by a thin film analyzer (F40, Filmetrics, San Diego, CA, USA).

3. Results and Discussion

The molar flow rates in the experiments can be calculated by Equations (1)–(3) [21,22]:

$$\ln\left(P_{\rm MO}\right) = a - b/T \tag{1}$$

where P_{MO} is the vapor pressure of TMGa, a = 8.07, b = 1703, T is the thermodynamic temperature of TMGa,

$$n_{\rm MO} = F \times P_{\rm MO} / [V_{\rm m} \times (P_{\rm hub} - P_{\rm MO})], \tag{2}$$

where n_{MO} is the molar flow rate of TMGa, *F* is the flow rate of carrier gas, $V_m = 22414 \text{ cm}^3/\text{mol}$, P_{bub} is the pressure inside the bubbler,

$$n_{\rm O} = F_{\rm O} / V_{\rm m},\tag{3}$$

where $n_{\rm O}$ is the molar flow rate of O₂, $F_{\rm O}$ is the flow rate of O₂. The VI/III ratios in the experiments are shown in Table 1.

Flow Rate for Ar Carrier Gas (sccm)	VI/III ratio (×10 ³)
5	66.9
15	22.3
30	11.2
45	7.4
60	5.6

Table 1. The VI/III ratios at various flow rates of Ar carrier gas.

3.1. Growth Rate Analysis

To investigate the growth rates, the thicknesses of the samples were measured by a thin film analyzer. The sample obtained with VI/III ratio of 5.6×10^3 is unsuitable for such analysis due to its excessively rough surface [18]. The growth rate showed a strong dependence on the VI/III ratio (Figure 1). Because the flow rate of oxygen was a constant, the growth rate was mainly limited by the flow rate of organometallic source. By increasing the flow rates of Ar carrier gas from 5 sccm to 45 sccm, the VI/III ratio decreased from 66.9×10^3 to 7.4×10^3 , and the growth rate improved from 0.26 to 1.98 µm/h.



Figure 1. Growth rates of the samples obtained with various VI/III ratios.

3.2. XRD Analysis

Figure 2 shows the XRD θ -2 θ scan patterns of β -Ga₂O₃ films grown with various VI/III ratios. For the film grown with VI/III ratio of 66.9 × 10³, except the diffraction peaks of Al₂O₃ substrate, only three peaks located at 18.76°, 38.10° and 58.84° could be observed, which related to β -Ga₂O₃ (-201), (-402), and (-603). It indicated that the thin film consisted of pure β -Ga₂O₃. By decreasing the VI/III ratio from 66.9 × 10³ to 11.2 × 10³, the three peaks of β -Ga₂O₃ were strengthened and sharpened. The crystallite sizes along the direction vertical to (-201) plane of the samples obtained with the VI/III ratios of 66.9 × 10³, 22.3 × 10³, and 11.2 × 10³ were calculated to be 11.2, 12.2, and 17.5 nm, respectively (by Scherrer equation). Larger crystallite sizes indicated lower defect density and an improvement of crystalline quality. Lower VI/III ratio was helpful to reduce the nuclei density in the initial stage of deposition process and enlarge the size of islands in the subsequent stage, which indicated that less defects occurred in island coalescence [23,24]. However, further decreasing the VI/III ratio caused crystalline quality degradation. For the film grown with VI/III ratio of 7.4 × 10³, the intensities of the three β -Ga₂O₃ peaks declined, and peaks related to β -Ga₂O₃ (401), (-601), (601), and (-801) were observed, indicating the polycrystalline structure of the film. The change in crystalline structure is caused by excessive nucleation rate with this VI/III ratio. At this nucleation rate, the deposited particles were unable to migrate to the appropriate lattice positions, and the films grew and oriented in unsuitable directions, which caused random growth. As for the sample obtained with VI/III ratio of 5.6×10^3 , the change in crystalline structure was obvious—15 peaks of β -Ga₂O₃ showed up. The crystallite sizes of the films grown with VI/III ratio of 7.4×10^3 and 5.6×10^3 were calculated to be 14.2 and 21.3 nm, respectively.



Figure 2. XRD θ -2 θ scan patterns of β -Ga₂O₃ films grown with various VI/III ratios: (**a**) 66.9 × 10³; (**b**) 22.3 × 10³; (**c**) 11.2 × 10³; (**d**) 7.4 × 10³; (**e**) 5.6 × 10³. Δ the peaks of the sapphire substrates.

3.3. AFM Analysis

To investigate the effects of VI/III ratios on the surface morphology of β -Ga₂O₃ films, AFM was carried out; the images are shown in Figure 3. The surface roughness of the films depended highly on the VI/III ratios. For the film grown with the VI/III ratios from 66.9×10^3 to 11.2×10^3 , root-mean-square (RMS) surface roughness increased from 3.71 to 7.83 nm. The hillocks on the surfaces enlarged and decreased in density, in good agreement with the XRD analysis. By decreasing the VI/III ratio to 7.4 × 10³, the surface roughness had little change, while the morphology changed greatly. Many wheat-like structures were observed, which means that excessive nucleation rate hindered particle migration and caused random growth. For the film grown with VI/III ratio of 5.6×10^3 , the roughness increased greatly, even reaching 56.3 nm (seven times higher than that of any other film), in accordance with its XRD pattern (Figure 2).



Figure 3. AFM images (5 μ m × 5 μ m) of β-Ga₂O₃ films grown with various VI/III ratios: (**a**) 66.9 × 10³; (**b**) 22.3 × 10³; (**c**) 11.2 × 10³; (**d**) 7.4 × 10³; (**e**) 5.6 × 10³.

3.4. FESEM Analysis

According to XRD analysis of all the films, the sample obtained with VI/III ratio of 11.2×10^3 was measured by FESEM. Figure 4 shows the top and cross-sectional views of FESEM images of the sample. The surface with minor defects is in accordance with the AFM image in Figure 3. The relatively smooth cross-sectional image indicates high film quality. In addition, the thickness measured by the cross-sectional view images is about 0.68 μ m.



Figure 4. FESEM images of β -Ga₂O₃ films grown with VI/III ratio of 11.2×10^3 : (a) Top-view; (b) cross-sectional view.

3.5. Raman Analysis

Figure 5 presents the Raman spectra of β -Ga₂O₃ films grown with various VI/III ratios. For comparison, the Raman spectra of the sapphire substrates is also shown in this figure. Except for the peaks related to the substrates, only one Raman peak related to β -Ga₂O₃ was observed. For the film grown with VI/III ratio of 66.9×10^3 , due to poor crystalline quality and a smooth surface, only one peak related to β -Ga₂O₃ was clearly observed. By decreasing the VI/III ratio, due to the change in crystalline quality and roughness, more peaks related to β -Ga₂O₃ showed up, which were gradually enhanced. However, when the VI/III ratio was decreased to 5.6×10^3 , owing to the excessively rough surface of the obtained sample, its surface area increased and its Raman spectrum changed greatly. Ten peaks related to β -Ga₂O₃ showed up and the peaks were enhanced greatly. The 10 peaks were divided into three categories [25–27]—the peaks located at 115, 147, 171, and 201 cm⁻¹ were attributed to libration and translation of tetrahedral-octahedra chains; the peaks located at 322, 349, and 476 cm⁻¹ were attributed to stretching and bending of GaO₄ tetrahedra. The Raman results confirmed that all the obtained films consisted of pure β -Ga₂O₃.



Figure 5. Raman spectra of β -Ga₂O₃ films grown with various VI/III ratios: (**a**) sapphire substrate; (**b**) 66.9 × 10³; (**c**) 22.3 × 10³; (**d**) 11.2 × 10³; (**e**) 7.4 × 10³; (**f**) 5.6 × 10³. *, the Raman peaks related to sapphire. Δ , the Raman peaks related to tetrahedral-octahedra chains. #, the Raman peaks related to GaO₆ octahedra. \Box , the Raman peaks related to GaO₄ tetrahedra.

4. Conclusions

In summary, β -Ga₂O₃ films were grown on sapphire (0001) substrates with various VI/III ratios by MOCVD. By varying the VI/III ratio, the crystalline quality obviously changed. For the film grown with VI/III ratios from 66.9×10^3 to 11.2×10^3 , the crystalline quality improved gradually, attributed to low nuclei density in the initial stage. However, further decreasing the VI/III ratio caused degradation of crystalline quality, and the morphological and Raman properties changed greatly, which was attributed to excessive nucleation rate. This work offers a feasible way to improve the crystalline quality of heteroepitaxial β -Ga₂O₃ films and is beneficial for device fabrication.

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References

- Higashiwaki, M.; Sasaki, K.; Murakami, H.; Kumagai, Y.; Koukitu, A.; Kuramata, A.; Masui, T.; Yamakoshi, S. Recent progress in Ga₂O₃ power devices. *Semicond. Sci. Technol.* **2016**, *31*, 034001. [CrossRef]
- 2. Goyal, A.; Yadav, B.S.; Thakur, O.P.; Kapoor, A.K.; Muralidharan, R. Effect of annealing on β-Ga₂O₃ film grown by pulsed laser deposition technique. *J. Alloy. Compd.* **2014**, *583*, 214–219. [CrossRef]
- 3. Kang, H.C. Heteroepitaxial growth of multidomain Ga₂O₃/sapphire (001) thin films deposited using radio frequency magnetron sputtering. *Mater. Lett.* **2014**, *119*, 123–126. [CrossRef]
- Nikolaev, V.I.; Pechnikov, A.I.; Stepanov, S.I.; Nikitina, I.P.; Smirnov, A.N.; Chikiryaka, A.V.; Sharofidinov, S.S.; Bougrov, V.E.; Romanov, A.E. Epitaxial growth of (-201) β-Ga₂O₃ on (0001) sapphire substrates by halide vapour phase epitaxy. *Mater. Sci. Semicond. Process* 2016, 47, 16–19. [CrossRef]
- 5. Liu, X.Z.; Guo, P.; Sheng, T.; Qian, L.X.; Zhang, W.L.; Li, Y.R. β-Ga₂O₃ thin films on sapphire pre-seeded by homo-self-templated buffer layer for solar-blind UV photodetector. *Opt. Mater.* **2016**, *51*, 203–207. [CrossRef]
- 6. Kumar, S.; Tessarek, C.; Christiansen, S.; Singh, R. A comparative study of β-Ga₂O₃ nanowires grown on different substrates using CVD technique. *J. Alloy. Compd.* **2014**, *587*, 812–818. [CrossRef]
- Sasaki, K.; Higashiwaki, M.; Kuramata, A.; Masui, T.; Yamakoshi, S. MBE grown β-Ga₂O₃ and its power device applications. *J. Cryst. Growth* 2013, *378*, 591–595. [CrossRef]
- Du, X.; Mi, W.; Luan, C.; Li, Z.; Xia, C.; Ma, J. Characterization of homoepitaxial β-Ga₂O₃ films prepared by metal–organic chemical vapor deposition. *J. Cryst. Growth* 2014, 404, 75–79. [CrossRef]
- 9. Terasako, T.; Kawasaki, Y.; Yagi, M. Growth and morphology control of β-Ga₂O₃ nanostructures by atmospheric-pressure CVD. *Thin Solid Films* **2016**, *620*, 23–29. [CrossRef]
- Ogita, M.; Saika, N.; Nakanishi, Y.; Hatanaka, Y. β-Ga₂O₃ thin films for high-temperature gas sensors. *Appl. Surf. Sci.* **1999**, *142*, 188–191. [CrossRef]
- 11. Chen, P.; Zhang, R.; Xu, X.F.; Zhou, Y.G.; Chen, Z.Z.; Xie, S.Y.; Li, W.P.; Zheng, Y.D. Oxidation of gallium nitride epilayers in dry oxygen. *Mater. Res. Soc. Internet J. Nitride Semicond. Res.* 2000, *5*, 866–872. [CrossRef]
- 12. Komiyama, H.; Shimogaki, Y.; Egashira, Y. Chemical reaction engineering in the design of CVD reactors. *Chem. Eng. Sci.* **1999**, *54*, 1941–1957. [CrossRef]
- 13. Parikh, R.P.; Adomaitis, R.A. An overview of gallium nitride growth chemistry and its effect on reactor design: Application to a planetary radial-flow CVD system. *J. Cryst. Growth* **2006**, *286*, 259–278. [CrossRef]
- 14. de Graaf, A.; van Deelen, J.; Poodt, P.; van Mol, T.; Spee, K.; Grob, F.; Kuypers, A. Development of atmospheric pressure CVD processes for high quality transparent conductive oxides. *Energy Procedia* **2010**, *2*, 41–48. [CrossRef]
- 15. Sbrockey, N.M.; Salagaj, T.; Coleman, E.; Tompa, G.S.; Moon, Y.; Kim, M.S. Large-area MOCVD growth of Ga₂O₃ in a rotating disc reactor. *J. Electron. Mater.* **2015**, *44*, 1357–1360. [CrossRef]
- 16. Lv, Y.; Ma, J.; Mi, W.; Luan, C.; Zhu, Z.; Xiao, H. Characterization of β-Ga₂O₃ thin films on sapphire (0001) using metal-organic chemical vapor deposition technique. *Vacuum* **2012**, *86*, 1850–1854. [CrossRef]
- Zhuo, Y.; Chen, Z.; Tu, W.; Ma, X.; Pei, Y.; Wang, G. β-Ga₂O₃ versus ε-Ga₂O₃: Control of the crystal phase composition of gallium oxide thin film prepared by metal-organic chemical vapor deposition. *Appl. Surf. Sci.* 2017, 420, 802–807. [CrossRef]
- 18. Alema, F.; Hertog, B.; Osinsky, A.; Mukhopadhyay, P.; Toporkov, M.; Schoenfeld, W.V. Fast growth rate of epitaxial β-Ga₂O₃ by close coupled showerhead MOCVD. *J. Cryst. Growth* **2017**, 475, 77–82. [CrossRef]
- 19. Takiguchi, Y.; Miyajima, S. Effect of post-deposition annealing on low temperature metalorganic chemical vapor deposited gallium oxide related materials. *J. Cryst. Growth* **2017**, *468*, 129–134. [CrossRef]
- Chen, Y.; Liang, H.; Xia, X.; Liu, Y.; Luo, Y.; Du, G. Effect of growth pressure on the characteristics of β-Ga₂O₃ films grown on GaAs (100) substrates by MOCVD method. *Appl. Surf. Sci.* 2015, 325, 258–261. [CrossRef]
- 21. Stringfellow, G.B. Organometallic Vapor-Phase Epitaxy: Theory and Practice, 2nd ed.; Academic Press: San Diego, CA, USA, 1999; pp. 163–169.

- 22. Lu, D.; Duan, S. *Metalorganic Vapor Phase Epitaxy Foundation and Application*, 1st ed.; Science Press: Beijing, China, 2009; pp. 11–46.
- 23. Vennegues, P.; Beaumont, B.; Haffouz, S.; Vaille, M.; Gibart, P. Influence of in situ sapphire surface preparation and carrier gas on the growth mode of GaN in MOVPE. *J. Cryst. Growth* **1998**, *187*, 167–177. [CrossRef]
- 24. Yang, T.; Uchida, K.; Mishima, T.; Kasai, J.; Gotoh, J. Control of initial nucleation by reducing the V/III ratio during the early stages of GaN growth. *Phys. Stat. Sol. A* **2000**, *180*, 45–50. [CrossRef]
- 25. Kumar, S.; Sarau, G.; Tessarek, C.; Bashouti, M.Y.; Hähnel, A.; Christiansen, S.; Singh, R. Study of iron-catalysed growth of β-Ga₂O₃ nanowires and their detailed characterization using TEM, Raman and cathodoluminescence techniques. *J. Phys. D Appl. Phys.* **2014**, *47*, 435101. [CrossRef]
- Rao, R.; Rao, A.M.; Xu, B.; Dong, J.; Sharma, S.; Sunkara, M.K. Blue shifted Raman scattering and its correlation with the [110] growth direction in gallium oxide nanowires. *J. Appl. Phys.* 2005, *98*, 094312. [CrossRef]
- Gao, Y.H.; Bando, Y.; Sato, T.; Zhang, Y.F.; Gao, X.Q. Synthesis, Raman scattering and defects of β-Ga₂O₃ nanorods. *Appl. Phys. Lett.* 2002, *81*, 2267–2269. [CrossRef]



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