J. Microelectron. Packag. Soc., 26(4), 113-118 (2019) https://doi.org/10.6117/kmeps.2019.26.4.113
Print ISSN 1226-9360 Online ISSN 2287-7525

Growth of α-Ga_2O_3 Epitaxial Films on Al_2O_3 by Halide Vapor Pressure Epitaxy

Daejang Lee[1], An-Na Cha[2], Junseong Park[2], Hogyun Noh[2], Youngboo Moon[1], and Jun-Seok Ha[2,3,†]

[1]UJL Inc. Advanced Institutes of Convergence Technology A1513, Kwangkyo-ro 145, Yeongtong-gu, Suwon-si, Gyeonggi-do, Korea
[2]School of Applied Chemical Engineering, Chonnam National University, Buk-gu, Gwangju 61186, Korea
[3]Optoelectronics Convergence Research Center, Chonnam National University, Buk-gu, Gwangju 61186, Korea
(Received December 16, 2019: Corrected December 24, 2019: Accepted December 28, 2019)

Abstract: In this study, we investigated the growth of single-crystallinity α-Ga_2O_3 thin films on c-plane sapphire substrates using halide vapor pressure epitaxy. We also found the optimal growth conditions to suppress the phase transition of α-Ga_2O_3. Our results confirmed that the growth temperature and partial pressure of the reactive gas greatly influenced the crystallinity. The optimal growth temperature range was about 460~510°C, and the α-Ga_2O_3 thin films with the highest crystallinity were obtained at a III/VI ratio of 4. The thickness and surface morphology of the thin films was observed by scanning electron microscopy. The film thickness was 6.938 μm, and the full width at half maximum of the ω-2θ scan rocking curve was as small as 178 arcsec. The optical band gap energy obtained was 5.21 eV, and the films were almost completely transparent in the near-ultraviolet and visible regions. The etch pit density was found to be as low as about 6.0×10^4 cm^{-2}.

Keywords: HVPE, α-Ga_2O_3, Al_2O_3, Heteroepitaxy, Single crystal

1. Introduction

Recently, gallium oxide (Ga_2O_3), an ultra-wide bandgap (UWBG) semiconductor, has been actively studied to replace GaN and SiC.[1-4] Owing to the ultra-wide energy bandgap, Ga_2O_3 can realize high-power devices with higher breakdown voltage and lower energy loss than GaN and SiC.[5-8]

Ga_2O_3 are grown in five phases (α, β, γ, ε, and δ) depending on growth parameters such as the growth temperature and pressure.[9]

Among them, the α-phase has a bigger bandgap (5.3 eV) than those of the other phases and is meta-stable at high temperatures (<600°C).[10] So far, the heteroepitaxial growth of α-Ga_2O_3 is possible on sapphire (α-Al_2O_3) substrates via mist chemical vapor deposition (mist-CVD),[11] halide vapor phase epitaxy (HVPE),[12,13] and molecular beam epitaxy (MBE).[14]

Growth of α-Ga_2O_3 via HVPE is type of chemical vapor deposition (CVD) method that has a rapid deposition rate and yields crystals of high purity. HVPE can grow thin films at a lower cost than other methods such as metal organic chemical vapor deposition (MOCVD) and MBE. Therefore, it is widely used in the III/V semiconductor industry.[15]

Previous studies have focused on heteroepitaxial growth on various substrates including sapphire substrates. Since α-Al_2O_3 have the same corundum structure as α-Ga_2O_3, Al_2O_3 is an optimal substrate for heteroepitaxial growth. Lattice mismatches between α-Ga_2O_3 and sapphire are about ~4.5% and ~3.3% along the a-axis and c-axis, respectively.[16,17] Also, Kaneko et al. reported that the semi-coherent growth of Ga_2O_3 on sapphire substrates is expected to prevent the occurrence of screw dislocations.[18] These studies show the possibility that α-Ga_2O_3 thin films with good crystallinity can be grown on sapphire substrates.

We have successfully grown α-Ga_2O_3 thin films having the single crystallinity among α-Ga_2O_3 films grown so far and exhibiting excellent physical properties.

2. Experimental

Fig. 1(a) is a schematic of the HVPE equipment used in the study. HVPE is a type of CVD method that reacts at atmospheric pressure in a horizontal reactor. In case of

†Corresponding author
E-mail: jsha@jnu.ac.kr

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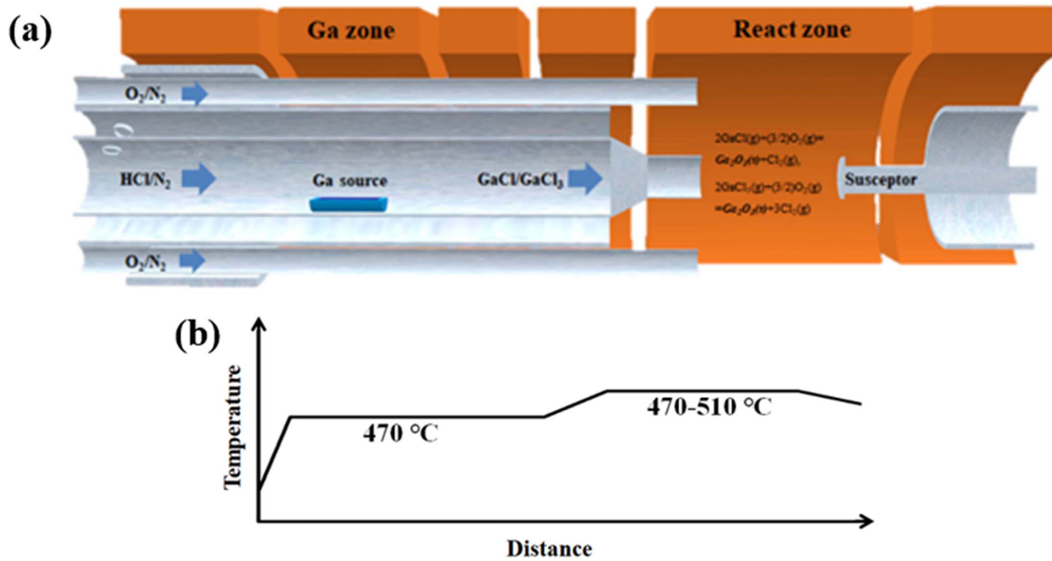

Fig. 1. (a) Schematic drawing of the HVPE system. (b) Process flow graph of temperature change with distance

HVPE, the precursor consisted of GaCl and O_2. GaCl was synthesized through a chemical reaction between metallic Ga (6N grade) and HCl gas (5N grade) at 470°C in the Ga source zone of the reactor. The partial pressures of HCl and O_2 were 0.25~0.55 kPa and 1~4 kPa, respectively. N^2 (6N grade) was used as the carrier gas. GaCl and O_2 were separately transferred to the growth zone, where an α-Al_2O_3 substrate was placed on a quartz glass susceptor. The HVPE equipment was divided into six sections, consisting of the Ga source zone in which Ga and HCl reacted and the growth zone in which α-Ga_2O_3 was grown by reacting GaCl and O_2. The remaining sections served as insulation sections. Fig. 1(b) shows the temperature change according to the distance in the reactor. The temperature of the Ga source zone was fixed at 470°C. The growth zone was heated to a temperature between 460 and 520°C under a N^2 flow and it contained O_2 at a partial pressure of 1 kPa. Growth time was fixed at 50 min.

The crystallinity of the resulting α-Ga_2O_3 thin films was analyzed by high-resolution X-ray diffraction (XRD). The surface morphology of the films was observed by scanning electron microscopy (SEM). The growth rate was determined by cross-sectional SEM. The structural quality was estimated by x-ray rocking curve (XRC) measurements. The impurity concentration was measured by secondary ion mass spectrometry (SIMS). The optical transmittance spectrum was utilized to determine the energy bandgap, and the baseline was measured with a double-side polished sapphire substrate. and a 45 wt% KOH solution was prepared and boiled at 65°C using a hot plate. Then, the α-Ga_2O_3 thin film was dipped into the solution for 60 min to confirm the density of defects.

3. Results and Discussion

We first studied the optimal temperature to suppress β phase in the temperature range of 470~510°C. Then, we found the optimal III/IV ratio to maximize crystallinity. In the case of Ga_2O_3, when the temperature exceeded a certain growth temperature, the α phase shifted to the β phase. The β phase peak was found in the region of about 38.8°.[19] Fig. 2(a) shows the XRD 2θ/θ scan profiles of the growth of α-Ga_2O_3 as a function of growth temperature. For α-Ga_2O_3 grown from 470 to 510°C, only peaks for α-Ga_2O_3 were found in the growth region and no peaks for β-Ga_2O_3 were observed. Moreover, peaks for α-Ga_2O_3 were not observed at temperatures below 460°C. When the growth temperature reached 520°C, β-Ga_2O_3 peaks were observed at about 38.3°. This result confirmed that transition from α phase to β phase occurred. Also, the stable temperature for α-Ga_2O_3 growth by HVPE was 470~510°C.

We also studied the change in crystallinity with respect to the growth zone temperature. Fig. 2(b) shows the XRC profiles of the α-Ga_2O_3 (0006) diffraction peaks. For Ga_2O_3 grown at 510°C, only the single crystal α phase was detected and excellent crystallinity at FWHM of 216 arcsec was observed for the (0006) reflection.

However, the crystallinity of α-Ga_2O_3 rapidly deteriorated at 520°C. The reason can be confirmed by the graph of Fig. 2(b) As shown in the graph, the α phase disappears at 520°C and the phase transitions to the polycrystalline β phase. Therefore, optimizing the growth temperature is an important factor for obtaining single crystallinity α-Ga_2O_3.

The growth temperature of pure α-Ga_2O_3 crystals is obtained differently depending on various growth methods.

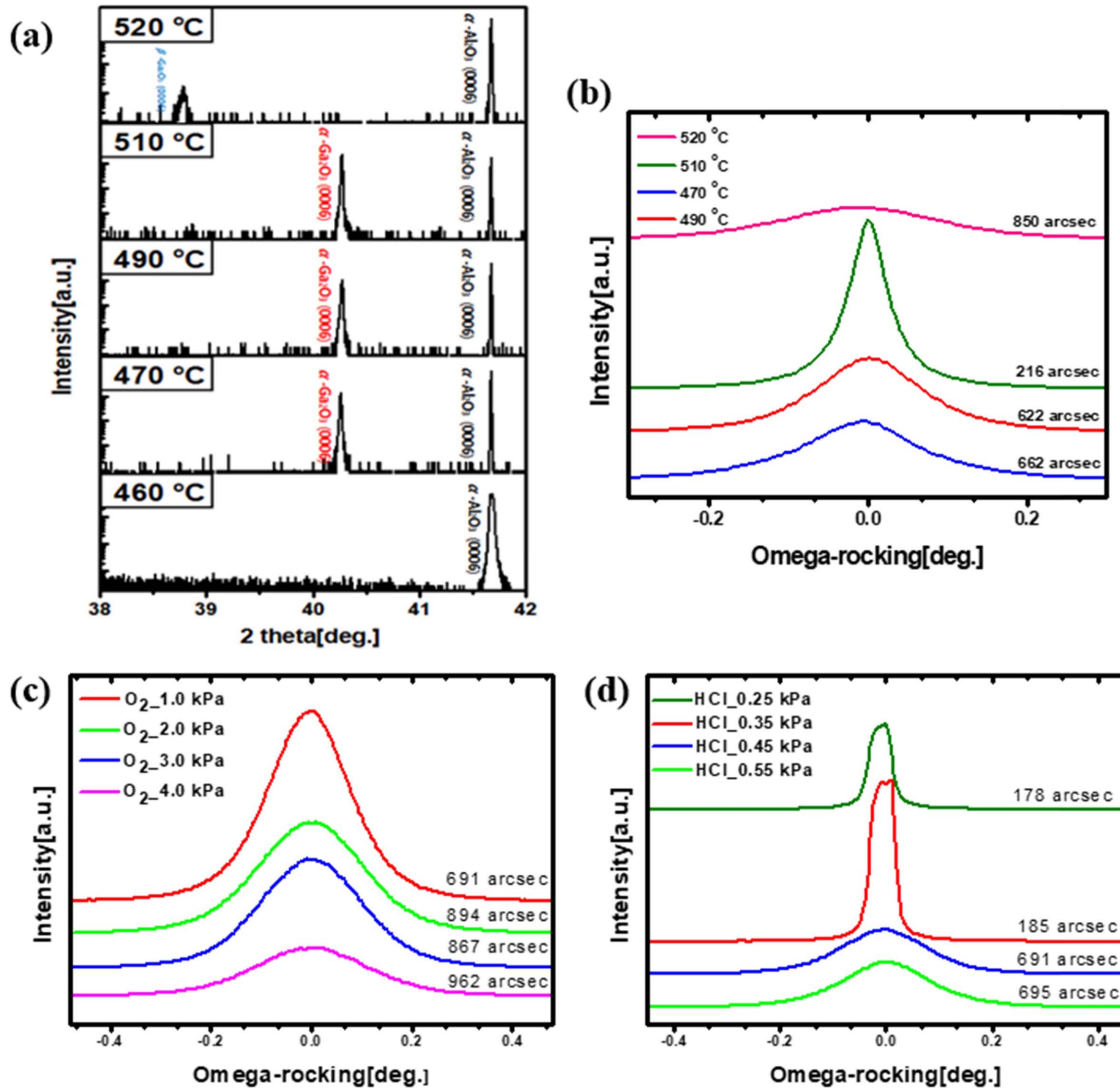

Fig. 2. XRD scan spectra of samples as functions of growth temperature. (a) 2θ/θ scan profile, (b) XRCs of an α-Ga_2O_3 film around (0006), (C) Thin film FWHM variation according to HCl partial pressure and (d) O_2 partial pressure.

Oshima and Fujita reported that using Mist-CVD, β-Ga_2O_3 was not grown from 470 to 630°C, and that only α-Ga_2O_3 was grown in this temperature range.[7] In contrast, when Ga_2O_3 films were grown using MBE on c-plane sapphire substrates in the same temperature range, β-Ga_2O_3 was found at about 38°.[20] Such a difference could originate not only from the growth temperature but also from the basic characteristics of each growth method.

Fig. 2(c) shows the results of the experiment to obtain optimal crystallinity through III/VI ratio control. First, we investigated the changes in crystallinity with respect to changes in P(HCl). P(O_2) was fixed at 1.00 kPa, while P(HCl) was varied from 0.25 to 0.55 kPa. Under constant P(O_2), FWHM decreased as P(HCl) decreased.

Second, Fig. 2(d) shows the change in FWHM with the change in P(HCl). P(HCl) was fixed at 0.45 kPa, while P(O_2) was varied from 1.00 to 4.00 kPa. Similar to the changes in crystallinity observed when P(HCl) was varied, the crystallinity tended to increase as the react gas partial pressure decreased. These results show that excess reactive gas interferes with the binding of $GaCl_3$ and O_2 and reduces crystallinity. These growth conditions may differ depending on the temperature of the Ga source zone, the flow rate of the carrier gas, and the capacity of the growth zone. Therefore, we studied the effect of flow rate of the carrier gas on the crystallinity, keeping the temperature of the Ga source zone constant at 470°C.

Fig. 3(a) shows an SEM image of a sample α-Ga_2O_3 thin film grown on a sapphire substrate. The surface of the thin film was mirror-like and transparent. The growth temperature was set at 510°C to suppress the formation of the β phase, and the III/VI ratio was fixed at 4 to ensure single crystallinity. The thickness of the grown film was about 6.891 μm, and no defects or pits were observed on the sur-

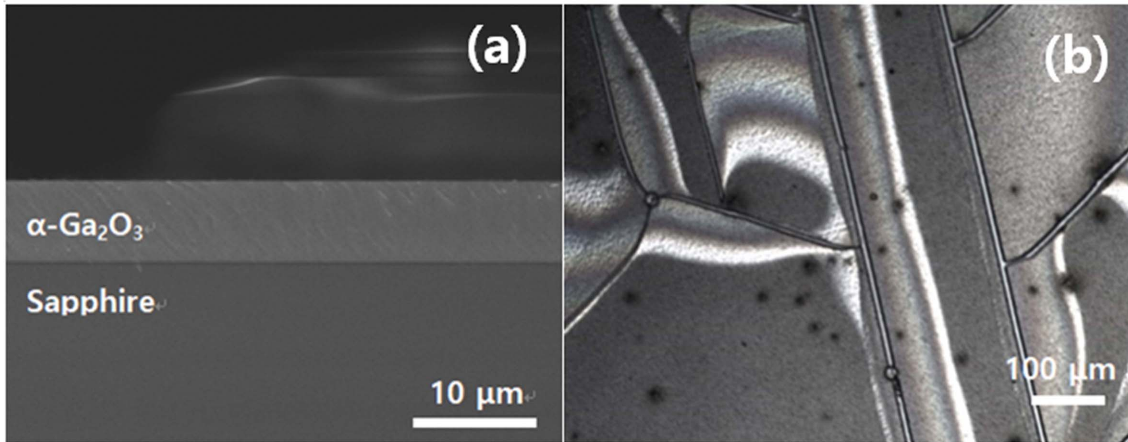

Fig. 3. Images of an α-Ga_2O_3 layer grown on a sapphire (0001) substrate: (a) cross-sectional image and (b) surface image with respect to etch pit density (EPD).

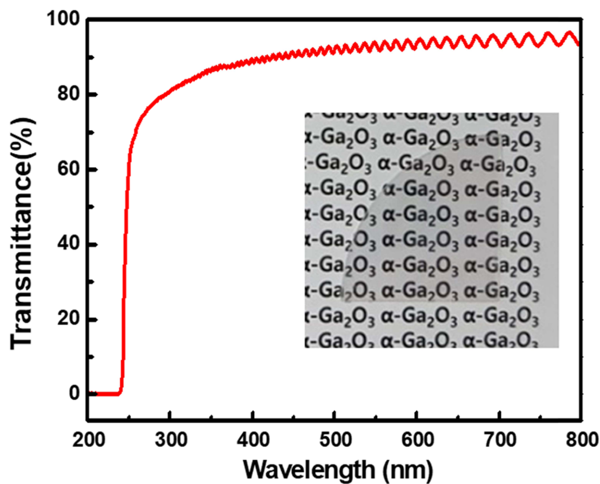

Fig. 4. Transmittance spectra and a photograph of α-Ga_2O_3. The inset shows the mirror-like surface.

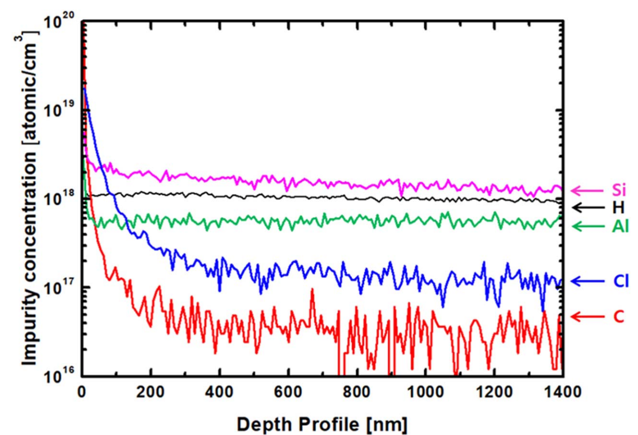

Fig. 5. Impurity concentrations in α-Ga_2O_3 measured by SIMS.

face. After the growth, when the sample was taken out of the reactor at a high temperature, a part of the thin film peeled off because of the difference between its thermal expansion coefficient and that of the substrate. Therefore, to prevent this peeling, the temperature was sufficiently lowered to 200°C before taking the sample out of the reactor.

Fig. 3(b) is an optical microscope image showing the crystallinity of α-Ga_2O_3 with respect to etch pit density (EPD). The EPD was found to be as low as about 6.0×10^4 cm^{-2}. To the best of our knowledge, this value is the lowest EPD obtained for α-Ga_2O_3 thin films grown by HVPE so far.

Fig. 4 shows the transmittance T of the thin film using a UV-vis spectrometer. Perfect absorption occurred in the region below 238 nm, and in the visible light region, transmittance was about 90%. We estimated the bandgap to be 5.21 eV from the $(h\upsilon\alpha)^2$-$h\upsilon$ plot. It was also confirmed that the α-Ga_2O_3 thin film grown on the double-side polished substrate was highly transparent (inset of Fig. 4).

Fig. 5 shows the impurity depth profiles measured in α-Ga_2O_3 grown on Sapphire substrate by SIMS. The elements [C], [H], [Si], [Al], and [Cl] were scanned. The concentrations of the typical impurities present in the α-Ga_2O_3 thin films were found to be as high as 10^{17} cm^{-3}. [C] and [H] were much lower than the reported values ([H]= 3×10^{19} cm^{-3}, [C] = 1×10^{19} cm^{-3}).[21)] Also, the concentration of [Cl] was found to be [Cl] = 1×10^{17} cm^{-3}. However, there is no clear evidence that Cl affects the electrical properties of α-Ga_2O_3. a report by Murakmi et al. has already revealed that Cl does not act in HVPE-grown β-Ga_2O_3 as a donor.[19]

4. Conclusions

In this study, α-Ga_2O_3 crystals with the single crystallinity reported so far were grown hetero-epitaxially on a c-plane sapphire substrate using HVPE. We modified the III/

VI ratio and growth temperature to grow a single crystallinity α-Ga_2O_3 thin film. As a result, the optimal growth temperature for α-Ga_2O_3 was 470~510°C.

However, at temperatures of 520°C or higher, α-Ga_2O_3 crystallinity greatly decreased due to phase transition to the β phase. The optimal temperature for single crystallinity α-Ga_2O_3 growth was 510°C. In addition, it was confirmed that the crystallinity changed according to the amount of reactive gas, and the optimal result was obtained at a III/VI ratio of 4. The crystallinity of α- Ga_2O_3 grown under optimal conditions was confirmed by XRC analysis. The FWHM of α- Ga_2O_3 was about 178 arcsec. EPD measurements using KOH solution were performed to confirm the defect density of the thin film; the EPD of the grown thin film was found to be about 6.0×10^4 cm^{-2}, which is relatively low. The result of SIMS measurements showed that [C] and [Cl] were relatively lower than those in α-Ga_2O_3 grown under the same growth conditions.

The optical transmittance of the thin film was higher than 90% in the visible and near-UV regions. The α-Ga_2O_3 epitaxial layer exhibited excellent crystallographic properties and smooth surface morphologies, and the bandgap was estimated to be 5.21 eV from the (hυα)2-hυ plot. The thickness of the grown thin film was about 6.891 μm. We confirmed that growth of thin films with low impurity concentration and defect density is possible and the possibility of single crystal growth using HVPE.

Acknowledgments

This work was supported by Priority Research Centers Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Education, Science and Technology (2018R1A6A1A03024334) and Basic Science Research Capacity Enhancement Project through Korea Basic Science Institute (National research Facilities and Equipment Center) grant funded by the Ministry of Education. (Grant No. 2019R1A6C1010024)

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