crystals

MDPI

Article

High Thermal Stability of κ-Ga_2O_3 Grown by MOCVD

Junhee Lee, Honghyuk Kim, Lakshay Gautam and Manijeh Razeghi *

Center for Quantum Devices, Department of Electrical and Computer Engineering, Northwestern University, Evanston, IL 60208, USA; junlee2024@u.northwestern.edu (J.L.); honghyuk.kim@northwestern.edu (H.K.); lakshaygautam2025@u.northwestern.edu (L.G.)
* Correspondence: razeghi@northwestern.edu

Abstract: We report a high thermal stability of kappa gallium oxide grown on c-plane sapphire substrate by metal organic chemical vapor deposition. Kappa gallium oxide is widely known as a metastable polymorph transitioning its phase when subjected to a high temperature. Here, we show the kappa gallium oxide whose phase is stable in a high temperature annealing process at 1000 °C. These oxide films were grown at 690 °C under nitrogen carrier gas. The materials showed high electrical resistivity when doped with silicon, whereas the film conductivity was significantly improved when doped with both indium and silicon. This work provides a pathway to overcoming limitations for the advance in utilizing kappa gallium oxide possessing superior electrical characteristics.

Keywords: MOCVD; metal oxide; thermal stability of κ-phase; Ga_2O_3 polymorph

Citation: Lee, J.; Kim, H.; Gautam, L.; Razeghi, M. High Thermal Stability of κ-Ga_2O_3 Grown by MOCVD. *Crystals* **2021**, *11*, 446. https://doi.org/10.3390/cryst11040446

Academic Editor: Ray-Hua Horng

Received: 24 March 2021
Accepted: 18 April 2021
Published: 20 April 2021

1. Introduction

Gallium oxide (Ga_2O_3) has been regarded as a promising next-generation material for realizing future ultra-wide bandgap optoelectronics and/or electronics such as ultraviolet solar blind photodetectors (SBPD) or high-power transistors. Despite of its potential, a complicated nature of Ga_2O_3 requires further understanding in the structural and electronic properties to advance the application fields to the greater extend. Among five different polymorphic forms (α-, β-, γ-, δ-, and κ-) of Ga_2O_3, β-phase Ga_2O_3 has widely been studied, since it is the most thermally and chemically stable as compared to other structures [1,2]. Moreover, a recent development in fabricating single crystal β-Ga_2O_3 substrates has been boosting up the expectation for the realization of devices based on such material in near future [3]. Apart from this promising phase of Ga_2O_3, growing attention has also been given to the metastable phase of Ga_2O_3, which is widely known as ε- or κ-phase [4,5], since it exhibits similar properties with β-Ga_2O_3 such as a wide direct bandgap energy of approximately 4.8 eV. Furthermore, various alloys containing other elements such as magnesium, indium, and aluminum can be utilized to tune its bandgap within the ultraviolet C light (UVC) solar blind band (200–280 nm) [6–8]. More importantly, the κ-Ga_2O_3 has been reported to exhibit unique properties, ferroelectric behavior and large polarization, that other polymorphs do not possess [9,10]. For example, the κ-Ga_2O_3 is predicted to have a large spontaneous polarization value which is about three times larger than the one of aluminum nitride [9]. In spite of numerous advantages of κ-phase, little has been studied making use of κ-Ga_2O_3 in the application. This is mainly due to the fact that the κ-Ga_2O_3 transits its phase to the β-Ga_2O_3 if high temperature energy is applied in order to activate dopants and to decrease the defect density inside layers [2,3]. Thus, further advancement of employing κ-Ga_2O_3 cannot be made unless the phase transition at high temperature issue is solved. Herein, we report a high thermal stability of κ-Ga_2O_3 grown on c-plane sapphire substrate by metal organic chemical vapor deposition (MOCVD). The κ-Ga_2O_3 thin films can withstand a high temperature annealing process at 1000 °C without having a phase transition. Moreover, when the materials are doped with both

silicon and indium, the improvement in electrical properties has been observed. This work provides a pathway to overcome limitations for the advance in utilizing kappa gallium oxide possessing superior electrical characteristics.

2. Materials and Methods

We grow various structures listed in Table 1 under N_2 carrier gas using Trimethyl-gallium (TMGa), Trimethyl-indium (TMIn), pure H_2O vapor and Silane (SiH_4) as Ga, In, O and Si precursors, respectively. Ga_2O_3 growth was performed on c-plane sapphire substrates by AIXTRON AIX200/4 horizontal MOCVD reactor at the growth temperature of 690 °C and at the pressure of 50 mbar. The post thermal annealing process was carried out for 1 minute by either ex situ rapid thermal annealing (RTA) or in situ annealing within the MOCVD reactor [11]. The structural property and the corresponding phase of the as-grown and annealed Ga_2O_3 epilayers were investigated by high-resolution x-ray diffraction (HR-XRD). Field emission scanning electron microscopy (SEM), Hitachi S-4500, was utilized to analyze the surface morphology of samples and also to measure the thickness of respective Ga_2O_3 epilayers. Electrical characteristics, including resistivity, mobility, and carrier concentration, of the films were obtained by using Van der Pauw Hall technique at room temperature. Optical characterizations were performed by photoluminescence (PL) measurement using an Ar ion laser with excitation wavelength of 244 nm.

Table 1. Detail information about various growth structures. Nitrogen was used as a carrier gas during the growth.

Structure	Components	TMGa	TMIn	H_2O	SiH_4
Structure 1	Ga_2O_3 [Reference]	5 sccm (N_2)	0 sccm (N_2)	1600 sccm (N_2)	20 sccm (N_2)
Structure 2	Superlattice [Ga_2O_3 (30 s)/In_2O_3 (1 min)]	5 sccm (N_2)	70 sccm (N_2)	1600 sccm (N_2)	0
Structure 3	Superlattice [Ga_2O_3 (30 s)/In_2O_3 (1 min)]	5 sccm (N_2)	70 sccm (N_2)	1600 sccm (N_2)	20 sccm (N_2)

3. Results and Discussion

Figure 1 shows the XRD spectra of all the as-grown and annealed materials listed in Table 1. The corresponding phase of these as-grown epilayers is identified to be κ-phase (Figure 1a), aligning with the calculated (002), (004), and (006) planes, similar to the materials grown under H_2 carrier gas as reported in our prior studies [11,12]. However, after the annealing process at 1000 °C, we did not observe any phase transition from κ- to β-phase. The phase of annealed epilayers remained the same, as shown in Figure 1b, which is opposed to the annealed Ga_2O_3 films grown under H_2 [11]. This observation indicates a high thermal stability of κ-Ga_2O_3 epilayers grown under N_2 carrier gas.

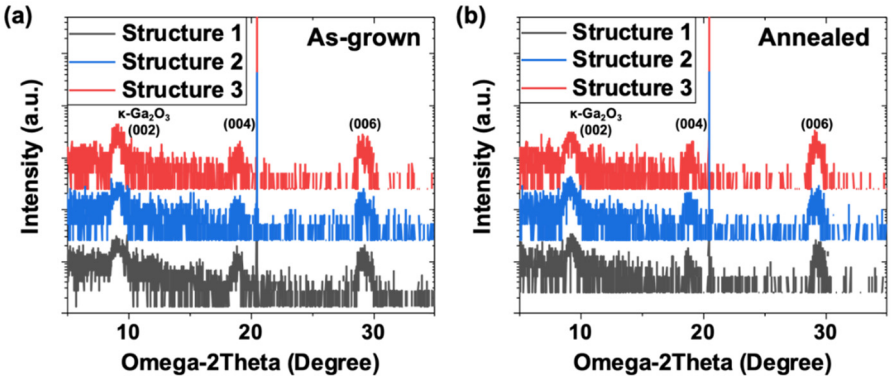

Figure 1. (**a**) XRD patterns from the various (**a**) as-grown Ga_2O_3 layers and (**b**) the annealed samples listed in Table 1.

Normalized PL spectra were measured from all of the various as-grown and annealed Ga_2O_3 films in Table 1. As shown in Figure 2a, we could not observe any change in PL peaks as comparing between before and after annealing. However, in our previous papers [11,12], we demonstrated that the difference in PL peaks depending on its phase has been found, exhibiting that the peak of κ-Ga_2O_3 is around 420 nm, while the β-phase has a 360 nm PL peak. In addition to the PL spectrum, even in the optical bandgap measurement, the materials grown under N_2 did not vary their optical bandgap upon annealing, which is in contrast to the materials grown under H_2 ambience [12]. Both optical characterization techniques confirm that the phase of as-grown materials is κ-phase and this phase can be maintained even after annealing at 1000 °C, suggesting the thermal stable κ-Ga_2O_3 epilayers can be grown under N_2 carrier gas.

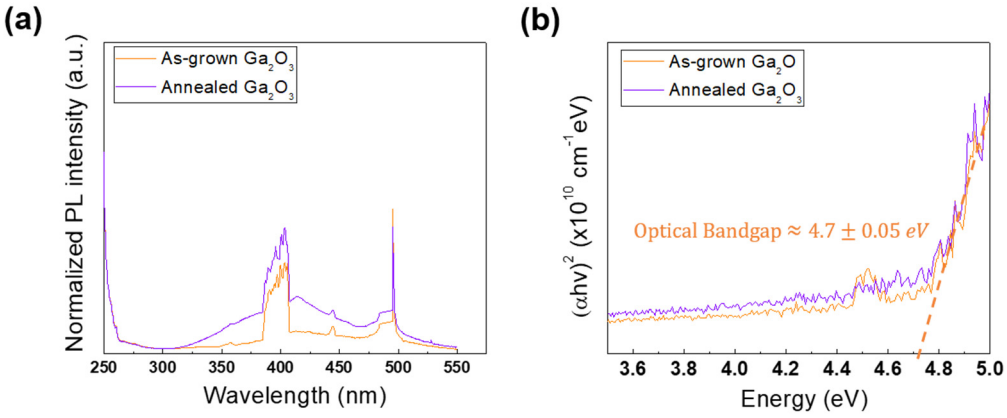

Figure 2. (**a**) Photoluminescence spectra from representative value of the as-grown and annealed Ga_2O_3 layers. (**b**) Transmission measurement data of as-grown and annealed Ga_2O_3 thin films.

Electrical characteristics of all epilayers listed in Table 1 are summarized in Table 2. The as-grown Ga_2O_3 layers without either silicon or indium dopant (Structure 1 and Structure 2) displayed extremely high resistivity, similar to the as-grown Ga_2O_3 grown under H_2 carrier gas [12]. However, when materials were doped with silicon and the presence of TMIn during the growth (Structure 3), the hall mobility of the sample was remarkably improved. It exhibited an electron concentration ($n \approx 2 \times 10^{17}$ cm^{-3}) similar to that grown under H_2, whereas the obtained hall electron mobility value was as low as around $\mu = 2$ $cm^2V^{-1}s^{-1}$. Regarding this phenomenon, we recently reported that the indium can play a role of a surfactant, causing the formation of less defective thin films, and thus resulting in the improvement in hall mobility [12]. On the other hand, contrary to our previous results, the annealing process did not induce an improvement of material conductivity. The Ga_2O_3 epilayers (Structure 1 and Structure 2) still presented a high resistivity while the co-doped Ga_2O_3 layer (Structure 3) had a slight increase in both carrier concentration ($n \approx 4 \times 10^{18}$ cm^{-3}) and hall mobility ($\mu = 4$ $cm^2V^{-1}s^{-1}$).

Table 2. Summary of the hall measurement data for the epitaxial layers listed in Table 1.

	Before Annealing		**After Annealing**	
	Hall Mobility	**Carrier Concentration**	**Hall Mobility**	**Carrier Concentration**
Structure 1	Highly resistive	Highly resistive	Highly resistive	Highly resistive
Structure 2	Highly resistive	Highly resistive	Highly resistive	Highly resistive
Structure 3	2 $cm^2/V{\cdot}s$	2×10^{17} cm^{-3}	4 $cm^2/V{\cdot}s$	4×10^{18} cm^{-3}

The thicknesses of the epilayers grown under different carrier gases were measured through the scanning electron microscope (SEM). The growth rates of respective epilayers under N_2 carrier gas were around 3 nm/min regardless of structures (Figure 3), which is

significantly lower than the layers grown under H_2 carrier gas (17 nm/min) [11,12]. In case of structure 3, the film thickness was approximately 600 nm when it was deposited under H_2. On the other hand, this was considerably reduced to 110 nm under N_2 ambient. The decrease of the growth rate under N_2 carrier gas can be interpreted as follows: according to the chemical reactions under either H_2 or N_2 carrier gas, the decomposition rate under N_2 is much less efficient than under H_2 carrier gas, leading to the low growth rate. This is also supported by the work [13], showing the TMGa is decomposed in different rates depending on the carrier gas. Due to the low decomposition speed, the undissolved organometallic complex would incorporate within epilayers giving the materials a high stable κ-phase. Furthermore, the incorporation of such organometallic complex makes the Si-doped materials compensated on the basis of the electrical properties displaying low carrier mobility and carrier concentration.

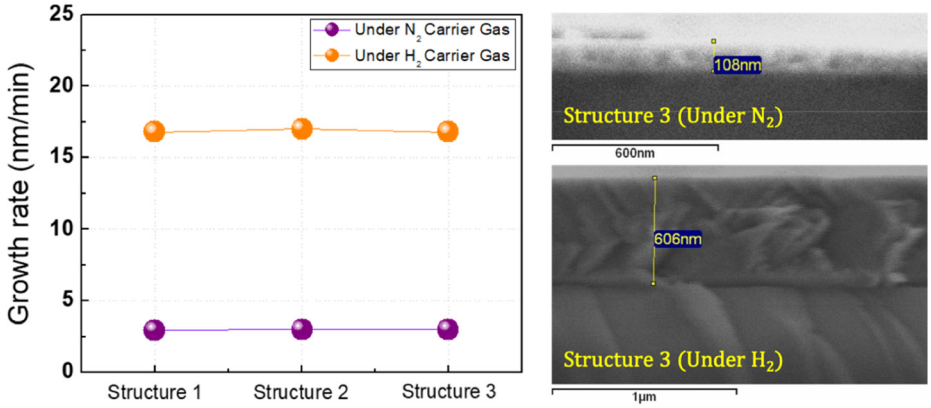

Figure 3. Growth rate variation for different structures and the corresponding SEM images of structure 3.

4. Conclusions

Highly thermal stable κ-Ga_2O_3 epilayers grown on c-plane sapphire substrate by MOCVD using N_2 carrier gas were demonstrated through the various characterization techniques such as structural (XRD and SEM), optical (PL and transmission), and electrical (Hall measurement) measurement. Structural as well as optical characterization data have confirmed that the metastable κ-phase Ga_2O_3 can withstand its phase even when subjected to the annealing at 1000 °C, which is opposed to the case grown under H_2 carrier gas where the phase transition occurred from κ- to β-phase. If the materials were grown with either silicon dopant or TMIn, both of the as-grown and annealed Ga_2O_3 films showed high resistive properties. However, the materials became conductive when doped with both silicon and indium. The growth rate under N_2 carrier gas was significantly decreased as compared to those grown under H_2, which can be attributed to different TMGa decomposition rates depending on the carrier gas. Despite the reduced growth rate, this observation suggests a pathway to maintain metastable κ-Ga_2O_3 possessing tremendous potential for further exploitation in the semiconductor industry.

Author Contributions: J.L. grew and characterized the materials and wrote the paper. H.K. helped with the X-ray measurement, and L.G. did the transmission measurement. M.R. provided the idea and supervised the whole research. All authors have read and agreed to the published version of the manuscript.

Funding: This work is supported by Air Force under agreement of FA9550-19-1-0410.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: This work is supported by Air Force under agreement of FA9550-19-1-0410. The authors would like to acknowledge the support and interest of Ali Sayir of USAF-AFMC AFMCAFOSR/RTB).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Roy, R.; Hill, V.G.; Osborn, E.F. Polymorphism of Ga_2O_3 and the System Ga_2O_3—H_2O. *J. Am. Chem. Soc.* **1952**, *74*, 719–722. [CrossRef]
2. Razeghi, M.; Park, J.H.; McClintock, R.; Pavlidis, D.; Teherani, F.H.; Rogers, D.J.; Magill, B.A.; Khodaparast, G.A.; Xu, Y.; Wu, J.; et al. A Review of the Growth, Doping, and Applications of β-Ga_2O_3 Thin Films. *Proc. SPIE* **2018**, *10533*, 105330R1-24.
3. Zhou, H.; Zhang, J.; Zhang, C.; Feng, Q.; Zhao, S.; Ma, P.; Hao, Y. A review of the most recent progresses of state-of-art gallium oxide power devices. *J. Semicond.* **2019**, *40*, 011803. [CrossRef]
4. Cora, I.; Mezzadri, F.; Boschi, F.; Bosi, M.; Čaplovičová, M.; Calestani, G.; Dódony, I.; Pécz, B.; Fornari, R. The real structure of ε-Ga_2O_3 and its relation to κ-phase. *CrystEngComm* **2017**, *19*, 1509–1516. [CrossRef]
5. Nikolaev, V.; Stepanov, S.; Pechnikov, A.V.; Shapenkov, S.; Scheglov, M.; Chikiryaka, A.; Vyvenko, O.F. HVPE Growth and Characterization of ε-Ga_2O_3 Films on Various Substrates. *ECS J. Solid State Sci. Technol.* **2020**, *9*, 045014. [CrossRef]
6. Anhar Uddin Bhuiyan, A.F.M.; Feng, Z.; Johnson, J.M.; Huang, H.L.; Hwang, J.; Zhao, H. MOCVD Epitaxy of ultrawide bandgap β-$(Al_xGa_{1-x})_2O_3$ with high-Al composition on (100) β-Ga_2O_3 substrates. *Cryst. Growth Des.* **2020**, *20*, 6722–6730. [CrossRef]
7. Hatipoglu, I.; Mukhopadhyay, P.; Alema, F.; Sakthivel, T.S.; Seal, S.; Osinsky, A.; Schoenfeld, W.V. Tuning the responsivity of monoclinic solar-blind photodetectors grown by metal organic chemical vapor deposition. *J. Phys. D Appl. Phys.* **2020**, *53*, 454001. [CrossRef]
8. Bi, X.; Wu, Z.; Huang, Y.; Tang, W. Stabilization and enhanced energy gap by Mg doping in ε-phase Ga_2O_3 thin films. *AIP Adv.* **2018**, *8*, 025008. [CrossRef]
9. Maccioni, M.B.; Fiorentini, V. Phase diagram and polarization of stable phases of $(Ga_{1-x}Inx)_2O_3$. *Appl. Phys. Express* **2016**, *9*, 041102. [CrossRef]
10. Nishinaka, H.; Miyauchi, N.; Tahara, D.; Morimoto, S.; Yoshimoto, M. Incorporation of indium into ε-gallium oxide epitaxial thin films grown via mist chemical vapour deposition for bandgap engineering. *CrystEngComm* **2018**, *20*, 1882–1888. [CrossRef]
11. Lee, J.; Kim, H.; Gautam, L.; He, K.; Hu, X.; Dravid, V.; Razeghi, M. Study of Phase Transition in MOCVD Grown Ga_2O_3 from κ to β Phase by Ex Situ and In Situ Annealing. *Photonics* **2021**, *8*, 17. [CrossRef]
12. Lee, J.; Kim, H.; Gautam, L.; Razeghi, M. Highly Conductive Co-Doped Ga_2O_3:Si-In Grown by MOCVD. *Coatings* **2021**, *11*, 287. [CrossRef]
13. Chen, Q.; Dapkus, P.D. On the Thermal Decomposition of Trimethylgallium—A Molecular Beam Sampling Mass Spectroscopy Study. *J. Electrochem. Soc.* **1991**, *138*, 2821. [CrossRef]