

Chemical Vapor Deposition of β -LiGaO₂ Films on Si(100) Using a Novel Single Precursor

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LiGaO₂ films have been grown on Si (100) substrates using a new single precursor [Li(OCH₂CH₂OCH₃)₂-Ga(CH₃)₂]₂ under high vacuum conditions (5×10^{-6} Torr). The [Li(OCH₂CH₂OCH₃)₂-Ga(CH₃)₂]₂ was synthesized and characterized by using spectroscopic methods and single-crystal X-ray diffraction analysis. The chemical composition, crystalline structure, and morphology of the deposited films were investigated by X-ray photoelectron spectroscopy, X-ray diffraction, and scanning electron microscopy. The results show that polycrystalline LiGaO₂ films preferentially oriented in the [010] direction can be deposited on Si (100) at 500–550 °C by metal organic chemical vapor deposition (MOCVD). The single precursor [Li(OCH₂CH₂OCH₃)₂-Ga(CH₃)₂]₂ has been found suitable for chemical vapor deposition of LiGaO₂ thin films on Si substrates.

Key Words : Metal organic chemical vapor deposition, LiGaO₂, Single precursor, GaN

Introduction

GaN and other III-nitride films have been generally grown on the (0001) plane of α -Al₂O₃ (sapphire) substrates in spite of the large lattice mismatch (~16% for GaN) and large difference in thermal expansion coefficients (the thermal expansion coefficient of GaN is 34% larger than that of α -Al₂O₃). Since commercial III-nitride single crystals are not available yet, alternative substrates such as 6H-SiC single crystals, 3C-SiC(111)/Si(111), *h*-AlN(0001)/Si(111), γ -LiAlO₂, and β -LiGaO₂ have been attractive. The lattice mismatches of these substrates with GaN are much smaller than that of α -Al₂O₃.

Among the alternative substrates, the β phase lithium gallate (β -LiGaO₂, hereafter LiGaO₂) single crystal is considered to be one of the most promising candidates for the epitaxial growth of GaN and other III-nitrides because the crystal is commercially available with relatively large size and has a very small lattice mismatch with GaN, and the (001) metallic surface of the crystal consists of Ga and Li only without oxygen.¹ The lattice mismatch between GaN (0001) and LiGaO₂(001) is less than 1%.² The crystal is orthorhombic with the cell dimensions $a = 0.5402 \pm 0.0001$ nm; $b = 0.6372 \pm 0.0001$ nm; and $c = 0.5007 \pm 0.0001$ nm.³ The crystal structure of LiGaO₂ is similar to the wurtzite structure. However, LiGaO₂ is not an exact wurtzite crystal but orthorhombic with distorted wurtzite structure because Li and Ga atoms have different sizes.⁴ In other words, the six-fold symmetry of the (0001) plane of wurtzite is reduced to two-fold symmetry of the (001) plane of LiGaO₂. Another characteristic of the LiGaO₂ crystal as substrate for III-nitrides is that it is a polar crystal. The space group of

LiGaO₂ is Pna2₁, which means that a LiGaO₂ crystal has a polarity along the *c*-axis. As reported in many articles,^{5–10} the polarity control of the GaN films is a challenging issue for device applications, because the roughness and some electrical properties of the as-grown GaN films are known to be affected to some extent by their polarity. Sumiya *et al.*⁹ reported that the polarity of GaN films grown on the (0001) plane of α -Al₂O₃ substrates with GaN or AlN buffer layers could be controlled by annealing the buffer layers. Using the LiGaO₂ as a substrate, however, one may easily control the polarity of the GaN films by alternating the (001) and (00 $\bar{1}$) planes of the substrate. In other words, Ga-terminated films would grow on the (001) plane of LiGaO₂ that has a cation-terminated surface,⁵ while N-terminated GaN films would grow on the (00 $\bar{1}$) plane of LiGaO₂. Thus LiGaO₂ would have the advantage of ease of the polarity control of successive GaN films over the nonpolar substrates such as α -Al₂O₃.

There are several reports on the growth of GaN films on LiGaO₂ crystals as substrates.^{2,11–14} Kung *et al.*¹¹ first reported on the MOCVD of monocrystalline GaN films on LiGaO₂. They observed that the quasi-two-dimensional transition occurred near 700 °C and that the FWHM of the GaN films deposited at 900 °C was 5 arcmin. Such results are comparable to those of the GaN films grown on α -Al₂O₃ substrates. Although articles on the growth of GaN films on LiGaO₂ substrates have been continually reported, no report has yet been published on the growth of GaN films on LiGaO₂ buffer films.

Recently, we developed several single precursors for MOCVD of LiGaO₂ films. In this paper, we report the growth of LiGaO₂ thin films on Si substrates using a novel hetero-bimetallic lithium organo-gallate complex [Li(OCH₂CH₂OCH₃)₂-Ga(CH₃)₂]₂ as a single precursor, and have found it to be a good source for MOCVD of LiGaO₂

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thin films. The synthesis and characterization of this lithium organo-gallate complex was reported in detail elsewhere.¹⁵

Experimental Section

Synthesis and Characterization of [Li(OCH₂CH₂OCH₃)₂-Ga(CH₃)₂]₂ (I). All manipulations were carried out under an inert atmosphere condition using a glove box or standard Schlenk techniques.¹⁶ All the chemicals and solvents were purified and dried by standard methods described in the literature.¹⁷ The ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer with chemical shifts referenced internally to benzene-*d*₆. FTIR spectra were recorded on a Nicolet Magna-IR 550 spectrometer as a Nujol mull between KBr plates.

To a solution of (CH₃)₂GaCl (1.48 g, 11.0 mmol) in 10 mL of hexane was slowly added a solution of lithium 2-methoxyethoxide (1.84 g, 22.0 mmol) in 10 mL of hexane by a pipet. The solution mixture was allowed to stir at ambient temperature for 3 hours. After filtering LiCl, the volatile organics were removed under reduced pressure. The recrystallization of the crude product by sublimation *in vacuo* resulted in colorless crystals [Li(OCH₂CH₂OCH₃)₂-Ga(CH₃)₂]₂ (I). Yield: 2.7 g, 93%. Mp: 112-114 °C. Anal. Calcd. (found) for C₁₆H₄₀O₈Ga₂Li₂: C, 37.40 (36.48); H, 7.85 (7.96). ¹H NMR (300.1 MHz, C₆D₆): δ 3.83 (t, 4H, -OCH₂CH₂OCH₃), 3.21 (t, 4H, -OCH₂CH₂OCH₃), 3.09 (s, 6H, -OCH₂CH₂OCH₃), -0.05 (s, 6H, GaCH₃). ¹³C NMR (75.5 MHz, C₆D₆): δ 76.20 (-OCH₂CH₂OCH₃), 62.07 (-OCH₂CH₂OCH₃), 58.44 (-OCH₂CH₂OCH₃), -8.79 (GaCH₃). IR (KBr): 2903 m, 2864 m, 1361 m, 1195 m, 1124 s, 1075 s, 1021 s, 915 s, 844 m, 724 s, 617 m, 419 s. MS (EI): *m/z* 449 (M⁺-CH₃).

The crystal structure of the precursor **I** was determined by single crystal X-ray crystallography. Single crystal X-ray diffraction data for the precursor **I** were collected on an Enraf-Nonius CAD4 diffractometer equipped with monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. The solutions of all structures were carried out by a combination of direct methods and Fourier techniques using SHELXS-86.¹⁸ The refinements of the structures of the precursor **I** by full-matrix least square method were based on 2312 unique reflections ($2\theta_{\max} = 50^\circ$, $>2\sigma$ (I)) using SHELXL-93.¹⁹ Anisotropic temperature factors were used for all nonhydrogen atoms. The volatilization and the stability of the precursor **I** were investigated by thermogravimetric and differential thermal analysis (TG/DTA). The TG/DTA of the precursor **I** was performed in an argon atmosphere under ambient pressure. The furnace was heated to 1000 °C at a heating rate of 5 °C min⁻¹. About 10 mg of the sample was generally used for the analysis.

Chemical Vapor Deposition and Characterization of LiGaO₂ Thin Films. A stainless-steel ultrahigh-vacuum (UHV) chamber was used for the growth of LiGaO₂ thin films. The reactor is pumped by ion and turbo-molecular pump combination achieving a base pressure of $< 1.0 \times 10^{-9}$ Torr. The gas line is pumped by an independent turbomolec-

ular pump. The Si substrates used for the film growth in this research were cut from n-type (100) wafers with resistivity in the range 1-5 Ω cm. The Si substrates were initially treated by a chemical cleaning process, which involves degreasing, HNO₃ boiling, NH₄OH boiling (alkali treatment), HCl boiling (acid treatment), rinsing in deionized water, and blow-drying with nitrogen, proposed by Ishizaka and Shiraki²⁰ to remove contaminants and grow a thin protective oxide layer on the surface. The substrates were introduced into UHV chamber by means of a load lock system.²¹ The temperature of the substrates was measured by an optical pyrometer through a 4.5 in. viewport in the chamber wall.

[Li(OCH₂CH₂OCH₃)₂-Ga(CH₃)₂]₂ used as a single source for LiGaO₂ thin films in this work was transferred into a glass bulb attached to the gas-handling system under high-vacuum condition ($< 1.0 \times 10^{-8}$ Torr) and was further purified by freeze-pump-thaw cycles using liquid nitrogen. The vapor of the precursor was introduced into the chamber through a variable leak valve (Granville-Phillips) and discharged from a nozzle located 3 cm above the substrate. Prior to the experiment, the chamber was pumped down to a pressure of low 10^{-9} Torr and then the substrate was mild-annealed at 650 °C for more than 5 hr to minimize out-gassing from the surface and the holder during deposition. Just before deposition, the substrate was heated up to 900 °C and annealed for 10 min to remove the oxide layer. With such a sample treatment, LiGaO₂ thin films were grown at temperatures of 400-800 °C under high vacuum condition (5×10^{-6} Torr).²² The duration of deposition ranged from 3 to 6 h.

Several analysis and characterization techniques were employed to investigate the LiGaO₂ thin films. X-ray photoelectron spectroscopy (XPS) was applied to study the compositions in the LiGaO₂ films. X-ray diffraction (XRD) was carried out to determine the crystallinity of the LiGaO₂ films. The surface morphology and growth rate were investigated by scanning electron microscopy (SEM).

Results and Discussion

Synthesis and Characterization of [Li(OCH₂CH₂OCH₃)₂-Ga(CH₃)₂]₂ (I). The dimer complex [Li(OCH₂CH₂OCH₃)₂-Ga(CH₃)₂]₂ was synthesized from (CH₃)₂GaCl with lithium 2-methoxyethoxide in hexane solution. The product was quantitatively obtained, and crystallized in the form of colorless crystals by sublimation *in vacuo* of the crude product. The ¹H and ¹³C NMR spectra of the precursor **I** confirm that the product is a pure dimer complex. The precursor **I** is highly soluble in organic solvents such as diethyl ether, THF, and hexane. The crystal structure of the precursor **I** was also determined by single crystal X-ray crystallography.

The molecular structure of the precursor **I** and its atomic numbering scheme are displayed in Figure 1. Thermal ellipsoids as drawn by ORTEP represent the 30% probability surfaces. H atoms are omitted for clarity. The precursor **I** is monoclinic, space group P2₁/n, with $a = 8.689$ (2) Å, $b =$

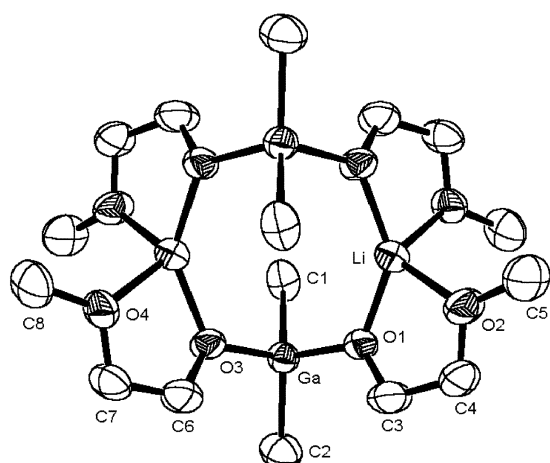


Figure 1. An ORTEP drawing of $[\text{Li}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2\text{Ga}(\text{CH}_3)_2]_2$.

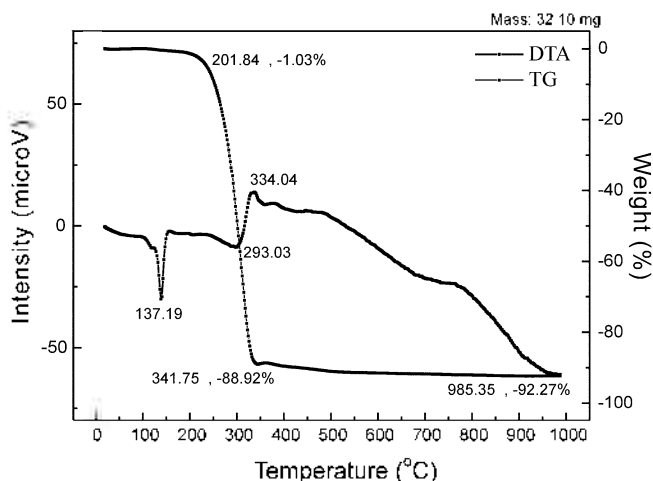


Figure 2. TG/DTA of $[\text{Li}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2\text{Ga}(\text{CH}_3)_2]_2$.

11.874 (3) Å, $c = 12.798$ (6) Å, $\beta = 93.87$ (3)°, and $Z = 4$. Figure 2 shows the TG/DTA plot of the precursor **I** under ambient pressure. From the TG curve it can be seen that a weight loss begins at 200 °C and completes by 340 °C. The DTA curve shows endothermic and exothermic peaks at 137 and 334 °C, attributed to the melting and decomposition of the precursor **I**, respectively.

Chemical Vapor Deposition of LiGaO_2 Thin Films. XRD patterns for the LiGaO_2 films on Si (100) as a function of deposition temperature are shown in Figure 3. The XRD pattern of the film deposited at 400 °C or lower shows either weak peaks or no peaks at all, indicating that amorphous LiGaO_2 films were obtained at these temperatures. The XRD pattern of the film at 450 °C clearly displays characteristic peaks of LiGaO_2 at $2\theta = 21.3^\circ$, 32.7° , 35.8° , 37.5° , and 57.8° that are attributed to LiGaO_2 (011), LiGaO_2 (120), LiGaO_2 (002), LiGaO_2 (121), and LiGaO_2 (040), respectively. It suggests that a polycrystalline LiGaO_2 film was obtained at this temperature. The XRD patterns of the LiGaO_2 films at 500–550 °C show a strong LiGaO_2 (040) peak with a weak LiGaO_2 (120) peak. This signifies that the LiGaO_2 films grown at 500–550 °C are polycrystalline and preferentially

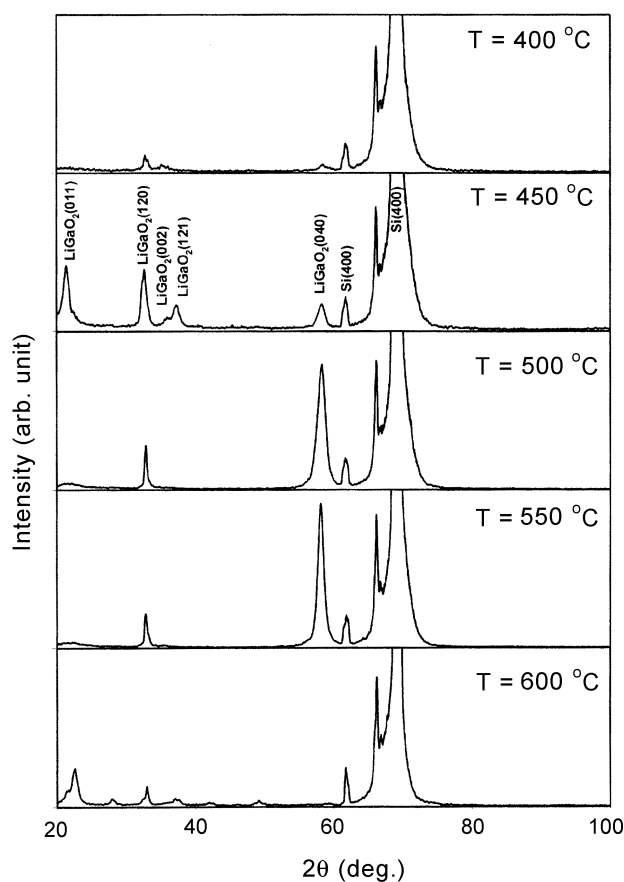


Figure 3. XRD patterns of LiGaO_2 films grown on Si(100) at 400–600 °C.

oriented to the [010] direction. However, the LiGaO_2 film at 600 °C shows several weak peaks, indicating that the film at 600 °C becomes less oriented.

Evolution of the surface morphology of the LiGaO_2 films was examined by scanning electron microscopy (SEM) as the growth temperature increased (Figure 4). The film grown at 400 °C appears smooth and uniform with no signs of

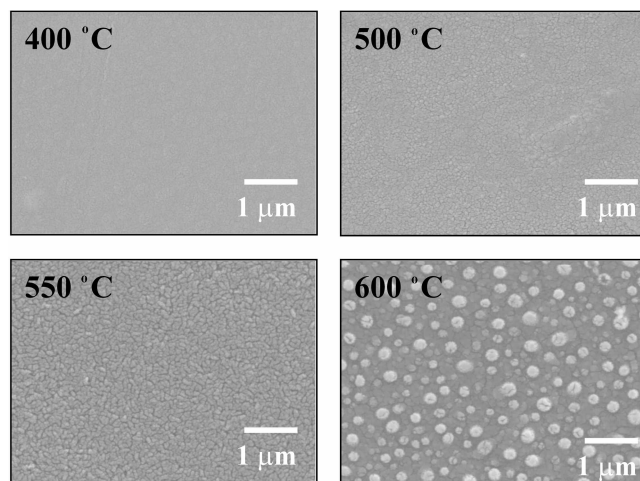


Figure 4. SEM images of LiGaO_2 films grown on Si(100) at 400–600 °C.

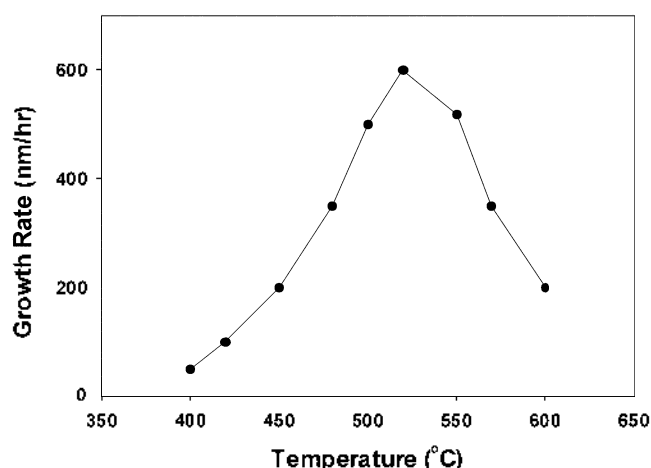


Figure 5. Growth rate of LiGaO₂ films on Si(100) at 400-600 °C.

granular crystallites. When the growth temperature was raised to above 500 °C, many crystalline grains were observed. The crystalline grains have become larger as the growth temperature increases. At the growth temperature of 600 °C, the surface morphology of the LiGaO₂ film becomes very rough and disordered.

The growth rates of the LiGaO₂ films as a function of deposition temperature were estimated by cross-sectional SEM (Figure 5). In the temperature range of 400-520 °C, the growth rate increases with temperature and the maximum growth rate is 600 nm/hr. At higher temperatures, the growth rate decreases with temperature probably due to decomposition of the precursor and subsequently evaporation of Li-

containing species from the substrates. XPS analysis was performed to determine the composition of the LiGaO₂ film on Si (100) deposited at 550 °C. Figure 6 shows the XP spectra of the as-received film and the same film cleaned by Ar⁺ ion sputtering. The spectra clearly display the photoelectron and Auger electron peaks for lithium, gallium, oxygen and carbon only. After the surface of the film was sputter etched by an Ar⁺ ion beam of 5 keV, the C 1s peak almost disappeared. It indicates that the carbon exists mostly in the surface region of the film. The ratio of the areas under Li 1s, Ga 3d and O 1s peaks of this film was the same as that of a LiGaO₂ single crystal. As a result, the XPS analysis evidently shows that the LiGaO₂ film is stoichiometric and has low levels of impurities.

Conclusions

LiGaO₂ films were grown on Si(100) by metal organic chemical vapor deposition under high vacuum conditions using the single precursor [Li(OCH₂CH₂OCH₃)₂Ga(CH₃)₂]₂. XRD analysis showed that LiGaO₂ films preferentially oriented in the [010] direction could be formed on Si(100) at 500-550 °C. The LiGaO₂ films, from XPS analysis, are also found to be stoichiometric and have low levels of impurities. From these results we have found that the volatile single precursor, [Li(OCH₂CH₂OCH₃)₂Ga(CH₃)₂]₂, with a Li:Ga:O ratio of 1:1:2, is suitable for MOCVD of LiGaO₂ films on Si(100) substrates.

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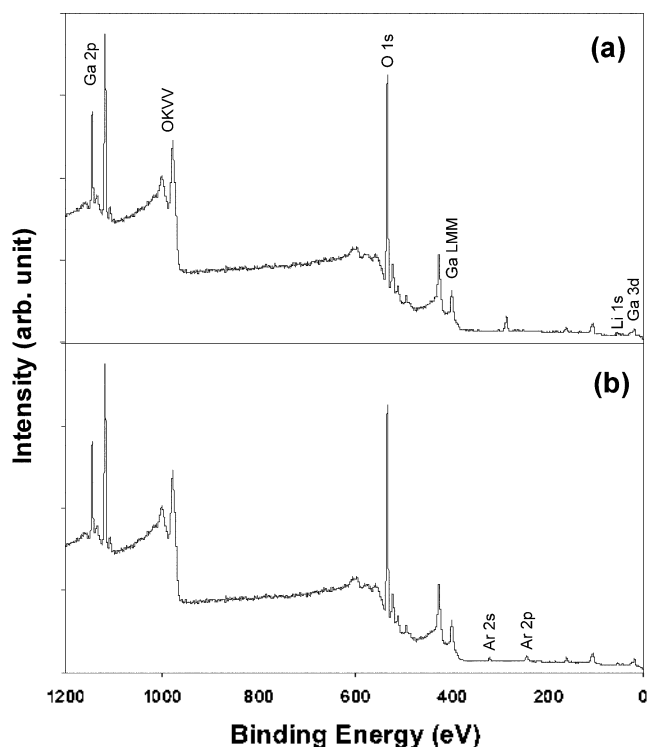


Figure 6. XP spectra of a LiGaO₂ film grown on Si(100) at 550 °C: (a) as-received; (b) Ar⁺ ion sputtered.

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