Chemical Vapor Deposition of β-$LiGaO_2$ Films on Si(100) Using a Novel Single Precursor

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$LiGaO_2$ films have been grown on Si (100) substrates using a new single precursor $[Li(OCH_2CH_2OCH_3)_2Ga(CH_3)_2]_2$ under high vacuum conditions (5×10^{-6} Torr). The $[Li(OCH_2CH_2OCH_3)_2Ga(CH_3)_2]_2$ 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 $LiGaO_2$ 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 $[Li(OCH_2CH_2OCH_3)_2Ga(CH_3)_2]_2$ has been found suitable for chemical vapor deposition of $LiGaO_2$ thin films on Si substrates.

Key Words : Metal organic chemical vapor deposition, $LiGaO_2$, Single precursor, GaN

Introduction

GaN and other III-nitride films have been generally grown on the (0001) plane of α-Al_2O_3 (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-Al_2O_3). 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-$LiAlO_2$, and β-$LiGaO_2$ have been attractive. The lattice mismatches of these substrates with GaN are much smaller than that of α-Al_2O_3.

Among the alternative substrates, the β phase lithium gallate (β-$LiGaO_2$, hereafter $LiGaO_2$) 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 $LiGaO_2$(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 $LiGaO_2$ is similar to the wurtzite structure. However, $LiGaO_2$ 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 $LiGaO_2$. Another characteristic of the $LiGaO_2$ crystal as substrate for III-nitrides is that it is a polar crystal. The space group of $LiGaO_2$ is $Pna2_1$, which means that a $LiGaO_2$ 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-Al_2O_3 substrates with GaN or AlN buffer layers could be controlled by annealing the buffer layers. Using the $LiGaO_2$ 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 $LiGaO_2$ that has a cation-terminated surface,[5] while N-terminated GaN films would grow on the $(00\bar{1})$ plane of $LiGaO_2$. Thus $LiGaO_2$ would have the advantage of ease of the polarity control of successive GaN films over the nonpolar substrates such as α-Al_2O_3.

There are several reports on the growth of GaN films on $LiGaO_2$ crystals as substrates.[2,11-14] Kung *et al.*[11] first reported on the MOCVD of monocrystalline GaN films on $LiGaO_2$. 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-Al_2O_3 substrates. Although articles on the growth of GaN films on $LiGaO_2$ substrates have been continually reported, no report has yet been published on the growth of GaN films on $LiGaO_2$ buffer films.

Recently, we developed several single precursors for MOCVD of $LiGaO_2$ films. In this paper, we report the growth of $LiGaO_2$ thin films on Si substrates using a novel hetero-bimetallic lithium organo-gallate complexe $[Li(OCH_2CH_2OCH_3)_2Ga(CH_3)_2]_2$ as a single precursor, and have found it to be a good source for MOCVD of $LiGaO_2$

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

Experimental Section

Synthesis and Characterization of [Li($OCH_2CH_2OCH_3$)$_2$-Ga(CH_3)$_2$]$_2$ (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 ^{13}C 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 $(CH_3)_2GaCl$ (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($OCH_2CH_2OCH_3$)$_2$-Ga(CH_3)$_2$]$_2$ (I). Yield: 2.7 g, 93%. Mp: 112-114 ℃. Anal. Calcd. (found) for $C_{16}H_{40}O_8Ga_2Li_2$: C, 37.40 (36.48); H, 7.85 (7.96). ^1H NMR (300.1 MHz, C_6D_6): δ 3.83 (t, 4H, -$OCH_2C\boldsymbol{H_2}OCH_3$), 3.21 (t, 4H, -$OC\boldsymbol{H_2}CH_2OCH_3$), 3.09 (s, 6H, -$OCH_2CH_2OC\boldsymbol{H_3}$), -0.05 (s, 6H, $GaC\boldsymbol{H_3}$). ^{13}C NMR (75.5 MHz, C_6D_6): δ 76.20 (-$OCH_2\boldsymbol{C}H_2OCH_3$), 62.07 (-$O\boldsymbol{C}H_2CH_2OCH_3$), 58.44 (-$OCH_2CH_2O\boldsymbol{C}H_3$), -8.79 ($Ga\boldsymbol{C}H_3$). 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^+-CH_3).

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 ($2\theta_{max} = 50^o$, $>2\sigma$ (**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 $LiGaO_2$ Thin Films. A stainless-steel ultrahigh-vacuum (UHV) chamber was used for the growth of $LiGaO_2$ 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 turbomolecular 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 Ωcm. The Si substrates were initially treated by a chemical cleaning process, which involves degreasing, HNO_3 boiling, NH_4OH boiling (alkali treatment), HCl boiling (acid treatment), rinsing in deionized water, and blow-drying with nitrogen, proposed by Ishizaka and Shiraki[20] 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($OCH_2CH_2OCH_3$)$_2$Ga(CH_3)$_2$]$_2$ used as a single source for $LiGaO_2$ 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 outgassing 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, $LiGaO_2$ 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 $LiGaO_2$ thin films. X-ray photoelectron spectroscopy (XPS) was applied to study the compositions in the $LiGaO_2$ films. X-ray diffraction (XRD) was carried out to determine the crystallinity of the $LiGaO_2$ films. The surface morphology and growth rate were investigated by scanning electron microscopy (SEM).

Results and Discussion

Synthesis and Characterization of [Li($OCH_2CH_2OCH_3$)$_2$-Ga(CH_3)$_2$]$_2$ (I). The dimer complex [Li($OCH_2CH_2OCH_3$)$_2$-Ga(CH_3)$_2$]$_2$ was synthesized from $(CH_3)_2GaCl$ 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 ^{13}C 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 $P2_1/n$, with a = 8.689 (2) Å, b =

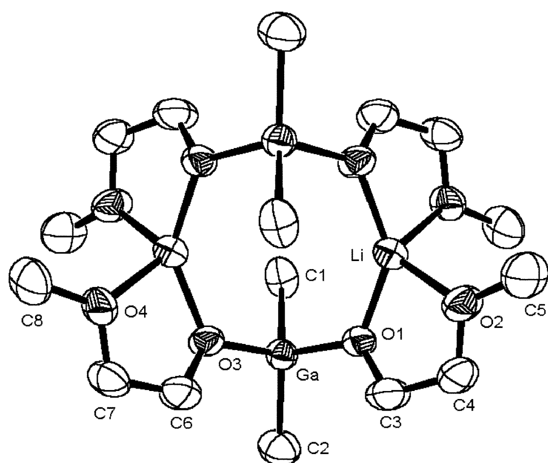

Figure 1. An ORTEP drawing of $[Li(OCH_2CH_2OCH_3)_2Ga(CH_3)_2]_2$.

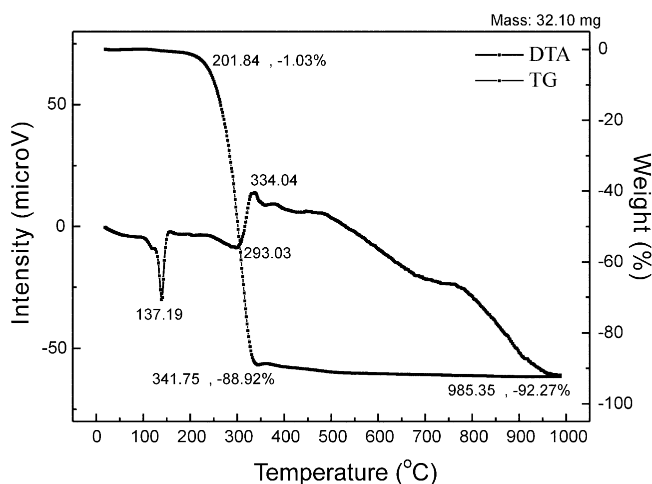

Figure 2. TG/DTA of $[Li(OCH_2CH_2OCH_3)_2Ga(CH_3)_2]_2$.

11.874 (3) Å, c = 12.798 (6) Å, β = 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 ºC and completes by 340 ºC. The DTA curve shows endothermic and exothermic peaks at 137 and 334 ºC, 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 ºC 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 ºC clearly displays characteristic peaks of $LiGaO_2$ at 2θ = 21.3°, 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 ºC 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 ºC are polycrystalline and preferentially oriented to the [010] direction. However, the $LiGaO_2$ film at 600 ºC shows several weak peaks, indicating that the film at 600 ºC becomes less oriented.

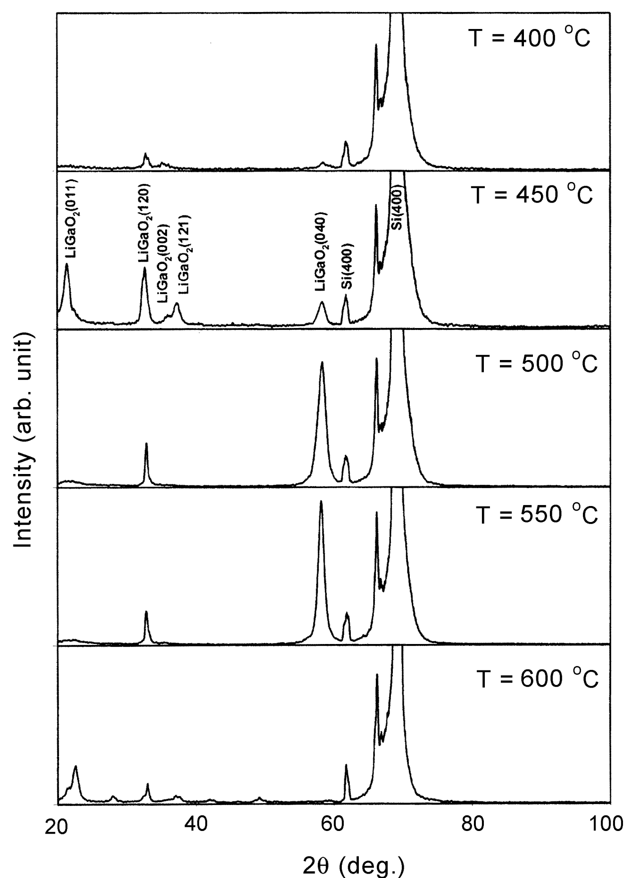

Figure 3. XRD patterns of $LiGaO_2$ films grown on Si(100) at 400-600 ºC.

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 ºC appears smooth and uniform with no signs of

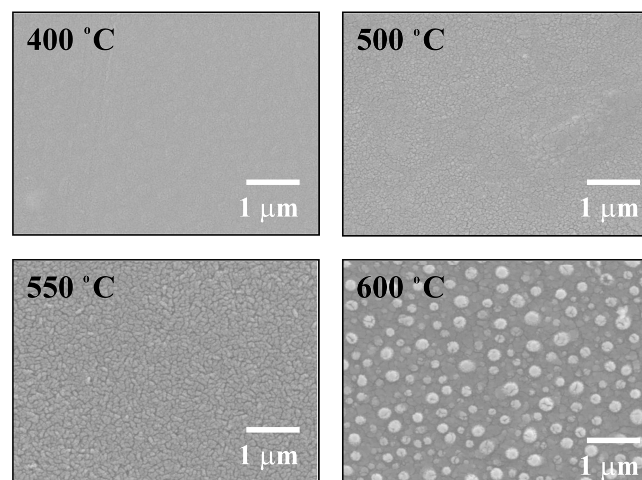

Figure 4. SEM images of $LiGaO_2$ films grown on Si(100) at 400-600 ºC.

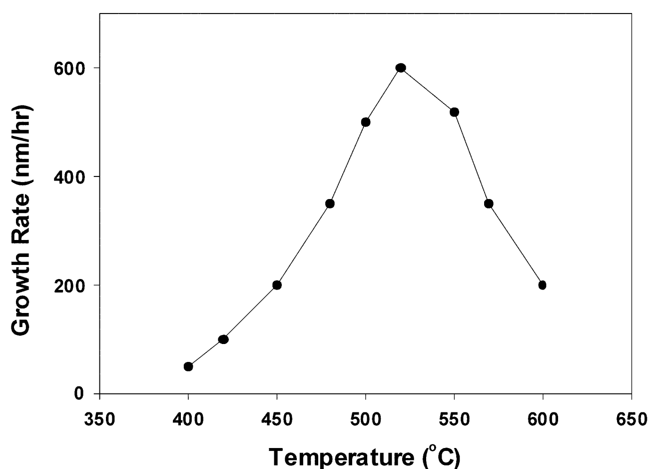

Figure 5. Growth rate of $LiGaO_2$ films on Si(100) at 400-600 °C.

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 $LiGaO_2$ film becomes very rough and disordered.

The growth rates of the $LiGaO_2$ 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 $LiGaO_2$ 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 $LiGaO_2$ single crystal. As a result, the XPS analysis evidently shows that the $LiGaO_2$ film is stoichiometric and has low levels of impurities.

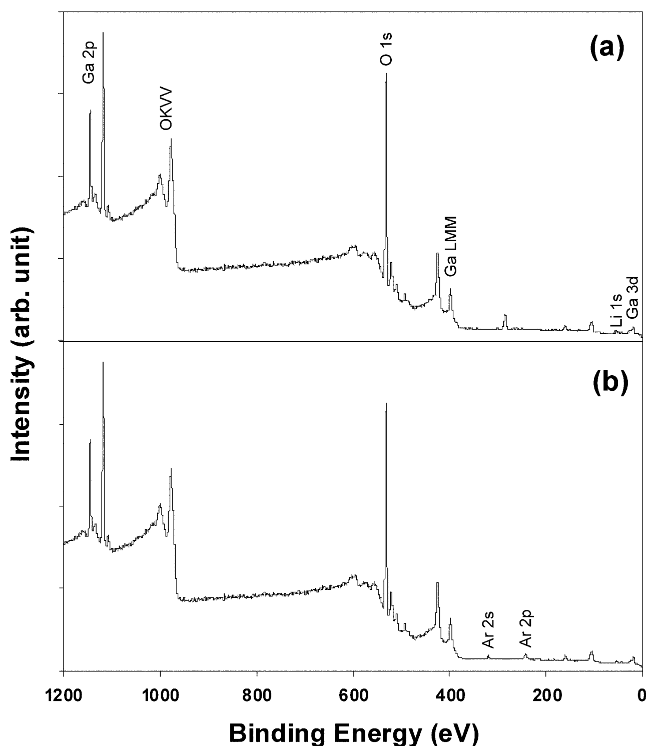

Figure 6. XP spectra of a $LiGaO_2$ film grown on Si(100) at 550 °C: (a) as-received; (b) Ar^+ ion sputtered.

Conclusions

$LiGaO_2$ films were grown on Si(100) by metal organic chemical vapor deposition under high vacuum conditions using the single precursor $[Li(OCH_2CH_2OCH_3)_2Ga(CH_3)_2]_2$. XRD analysis showed that $LiGaO_2$ films preferentially oriented in the [010] direction could be formed on Si(100) at 500-550 °C. The $LiGaO_2$ 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, $[Li(OCH_2CH_2OCH_3)_2Ga(CH_3)_2]_2$, with a Li:Ga:O ratio of 1:1:2, is suitable for MOCVD of $LiGaO_2$ films on Si(100) substrates.

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