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# Annealing effects on the properties of $Ga_2O_3$ thin films grown on sapphire by the metal organic chemical vapor deposition

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**Abstract**

We have prepared the gallium oxide ($Ga_2O_3$) thin films on sapphire substrates by the metal organic chemical vapor deposition (MOCVD) technique. We have compared the two films with and without the thermal annealing by using the X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and the photoluminescence (PL) spectra. Postdeposition annealing of amorphous $Ga_2O_3$ films was found to increase the degree of crystallization and the surface roughness. The PL emission intensities of bands in the blue–green and the ultraviolet regions increased by the thermal annealing.
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## 1. Introduction

Gallium oxide ($Ga_2O_3$) is one of the most promising materials as a metal oxide gas sensor [1–3] because it exhibits an n-type semiconductor property in the high temperature range over 600 °C due to the deficiency of oxygen in the crystal and an electrical conductivity appears owing to excess bonds (electrons) instead of lattice bonds, and besides it is a stable and monoclinic β-$Ga_2O_3$ in the high temperature [4,5]. Furthermore, crystals of β-$Ga_2O_3$ have recently attracted considerable attention as materials for the new generation of optoelectronic devices [6–12], since the crystals are transparent in a wide range of ultraviolet (UV) down to 280 nm and they are potentially electro-conductive. Excellent chemical and physical stability is also an advantage of this material.

Many techniques have been employed to prepare the $Ga_2O_3$ films, e.g. evaporation [13], sol–gel process [14], sputtering [15–17], pulsed laser deposition [18], molecular beam epitaxy [19], and oxidation of surfaces of GaAs [20], CoGa [21–23], and GaN [24]. However, although the metal organic (MO) chemical vapor deposition (CVD) method has an advantage of more flexibility, good step coverage, and uniformity, there are only few reports on the growth of $Ga_2O_3$ thin films by the MOCVD technique using the precursors of $Ga(hfac)_3$, $Ga[OCH(CF_3)_2]_3^{\bullet}$ $HNMe_2$, and $[Ga(\mu\text{-}O\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2]_2$ [25–27].

In this research, we have deposited the $Ga_2O_3$ thin films on sapphire substrates using a conventional precursor of trimethylgallium (TMGa). Subsequently,

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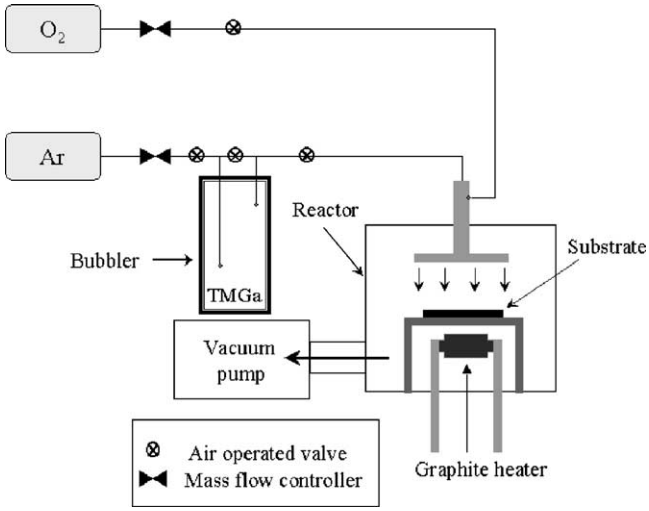


Fig. 1. Schematic diagram of the MOCVD reactor for growing the $Ga_2O_3$ thin films.

we have annealed the $Ga_2O_3$ thin films at a higher temperature of 1050 °C and have investigated the effect of annealing on three-dimensional gallium oxide film morphology using plan-view and cross-sectional scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), and atomic force microscopy (AFM). Since there is rare report on emission from $Ga_2O_3$ films produced by using MOCVD, the optical properties of the films were studied via photoluminescence (PL).

## 2. Experimental

The $Ga_2O_3$ films were grown on sapphire (0 0 0 6) substrates. The substrate was cleaned in acetone for 10 min, then rinsed by deionized water for 1 min. A schematic diagram of the MOCVD reactor used in our experiments is described in Fig. 1. TMGa and $O_2$ were used as sources. High-purity Ar passed through the TMGa bubbler, which had been maintained at the temperature of −5 °C, and delivered the TMGa vapor to the reactor. The $Ga_2O_3$ film was synthesized by supplying $O_2$ and Ar carrier gases with the flow rate of 30 and 30 sccm, and the reaction temperature was set to 550 °C. As-deposited film exhibited a uniform and smooth surface.

After the deposition of the $Ga_2O_3$ film, samples were annealed in a quartz tube furnace at a temperature of 1050 °C for 1 h in air ambient. The structural characteristics of the films were analyzed by XRD (Philips, CM20T, 200 kV) using Cu Kα1 radiation ($\lambda = 0.154056$ nm) and SEM (Hitachi S-4200). The surface roughness was measured using an AFM (Nanoscope III, Digital Instruments) with a scan size

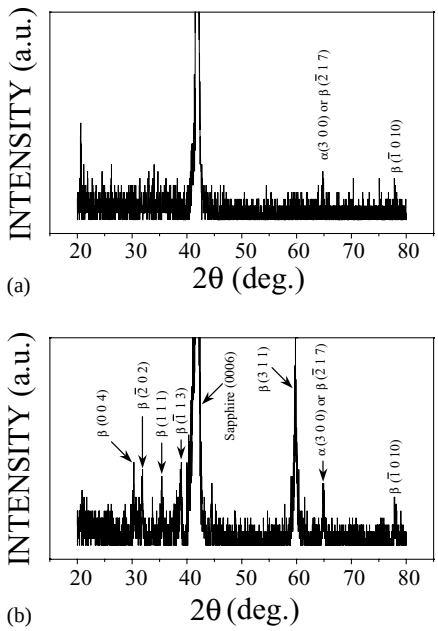


Fig. 2. XRD patterns of the (a) as-deposited and (b) 1050 °C-annealed $Ga_2O_3$ deposits.

of 10 μm × 10 μm. PL measurements were carried out at room temperature with a Shimadzu fluorescence spectrophotometer (RF-5301PC). The excitation light was the monochromatic light from a xenon short arc lamp with a wavelength of $\lambda = 250$ nm.

## 3. Results and discussion

In order to investigate the effect of thermal annealing on the crystallinity of $Ga_2O_3$ thin film grown on sapphire substrates, we have performed an XRD analysis. The $Ga_2O_3$ film was grown at a temperature of 550 °C and the thickness of $Ga_2O_3$ films was measured to be about 200 nm.

Fig. 2a shows the XRD diffraction peaks of the as-deposited $Ga_2O_3$ deposits. Although we suppose that the deposits are close to the amorphous phase due to the absence of a strong $Ga_2O_3$ diffraction peak, there are very weak diffraction peaks, corresponding to the $Ga_2O_3$ structure. Within experimental error, the lines observed in this diffractogram are found to coincide

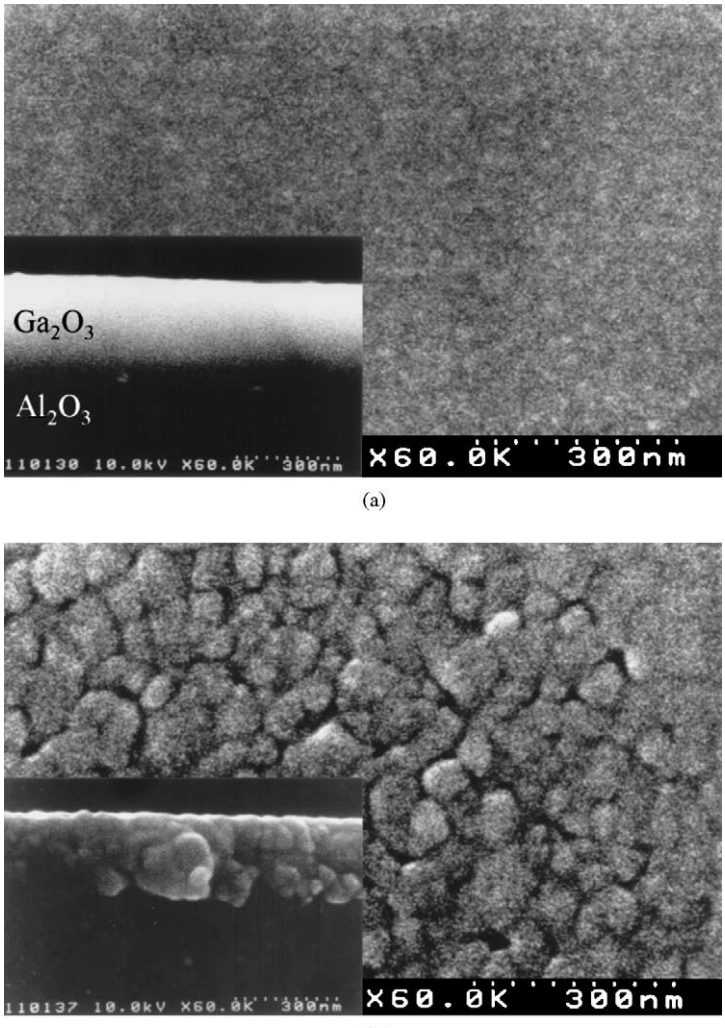


Fig. 3. Plain-view SEM images of (a) as-deposited and (b) annealed $Ga_2O_3$ thin films (Inset: cross-sectional SEM images of $Ga_2O_3$ thin films).

with (3 0 0) peak of α-$Ga_2O_3$ or ($\bar{2}$ 1 7) peak of β-$Ga_2O_3$, and ($\bar{1}$ 0 10) peaks of β-$Ga_2O_3$ (JCPDS 11-370). The α-$Ga_2O_3$ is metastable and has a hexagonal corundum structure and the stable β-$Ga_2O_3$ phase has a monoclinic structure [28]. The existence of the $Ga_2O_3$ peaks indicates the production of $Ga_2O_3$ deposits on sapphire substrates. We infer from XRD data that the deposits are crystallographically amorphous or contain very small crystallites.

Fig. 2b shows the diffraction peaks of the 1050 °C-annealed $Ga_2O_3$ deposits, indicating that the lines observed in this diffractogram are found to coincide with (0 0 4), ($\bar{2}$ 0 2), (1 1 1), ($\bar{1}$ 1 3), (3 1 1) of β-$Ga_2O_3$, (3 0 0) peak of α-$Ga_2O_3$ or ($\bar{2}$ 1 7) peak of β-$Ga_2O_3$, and ($\bar{1}$ 0 10) peaks of β-$Ga_2O_3$ (JCPDS 11-370). The existence of the β-$Ga_2O_3$ peaks indicates the production of β-$Ga_2O_3$ deposits on sapphire substrates. Since more $Ga_2O_3$ diffraction peaks become clearly observed after the thermal annealing, we reveal that the crystallinity of $Ga_2O_3$ films is improved with the thermal annealing at a temperature of 1050 °C.

Fig. 3a and b show the SEM images of $Ga_2O_3$ thin films, respectively, which are as-deposited and annealed at 1050 °C. The plain-view SEM images indicate that the grain-like structures begin to appear on top of the $Ga_2O_3$ thin films after the thermal annealing. The cross-sectional SEM images also indicate that although no clear grain boundaries are found inside the as-deposited $Ga_2O_3$ thin films, the grain-like structure appears by the thermal annealing. Based on the XRD data, we surmise that the grain-like structures in the SEM images are the grains associated with β-$Ga_2O_3$.

In order to investigate the surface roughness of the $Ga_2O_3$ films grown on sapphire substrates, we have performed an AFM analysis. Fig. 4a and b shows the

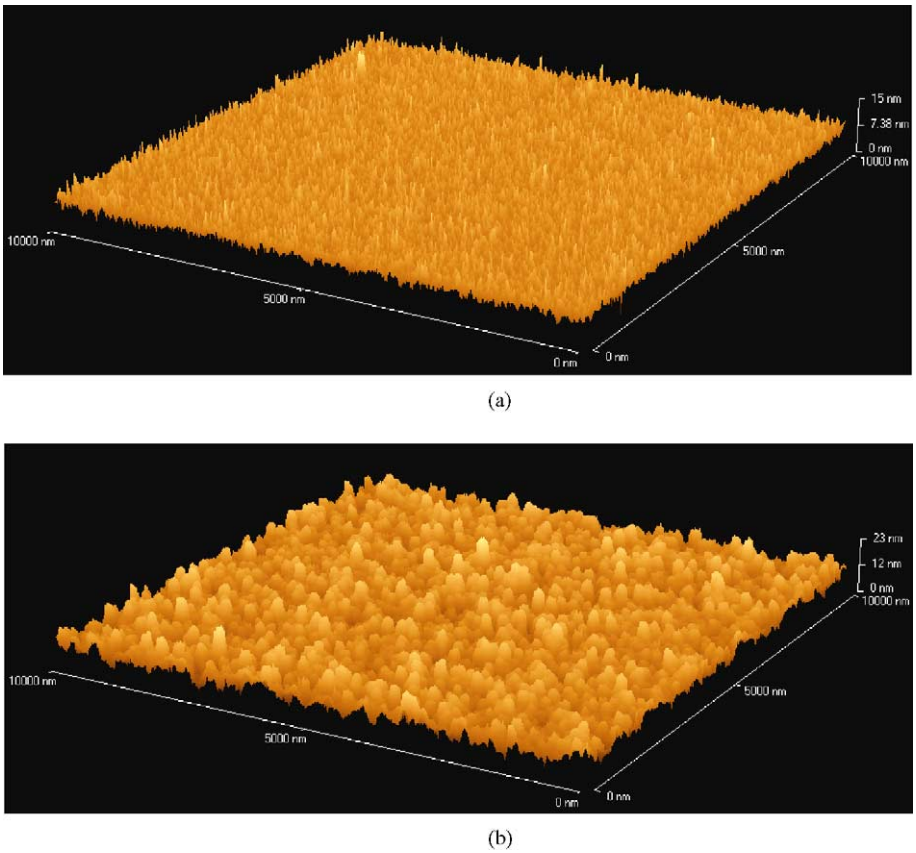


Fig. 4. AFM images representing the surface morphology of (a) as-deposited and (b) annealed $Ga_2O_3$ film.

AFM topographies representing the surface morphology of as-deposited and 1050 °C-annealed $Ga_2O_3$ film, respectively, indicating that the grain size on top of the $Ga_2O_3$ film increase with the thermal annealing. The root mean square (rms) surface roughnesses of the as-deposited and 1050 °C-annealed $Ga_2O_3$ films, respectively, are 1.15 and 2.28 nm, indicating that the surface of annealed $Ga_2O_3$ films is more rough than those of the as-deposited $Ga_2O_3$ films. We surmise that the surface becomes rougher with increasing the grain size due to the enlarged grain on top of the films, and thus the AFM images agree with the SEM images.

Fig. 5 shows the PL spectra of as-deposited and 1050 °C-annealed $Ga_2O_3$ films, which are recorded at room temperature (300 K). The dominant emission from both films is a band located at a wavelength of around 466 nm, corresponding to the energy of about 2.667 eV in the blue–green (BG) region. Since the samples annealed in reduction atmosphere is in favor of the formation of oxygen vacancies and blue emission was enhanced, while samples heated in $O_2$ atmosphere is in favor of the formation of Ga vacancies, which showed a dominant green emission [29], we surmise that the air ambient in our experiments is in favor of the neutral atmosphere, contributing to the BG emission. Further systematic study is underway in order to reveal the mechanism of the observed BG emissions.

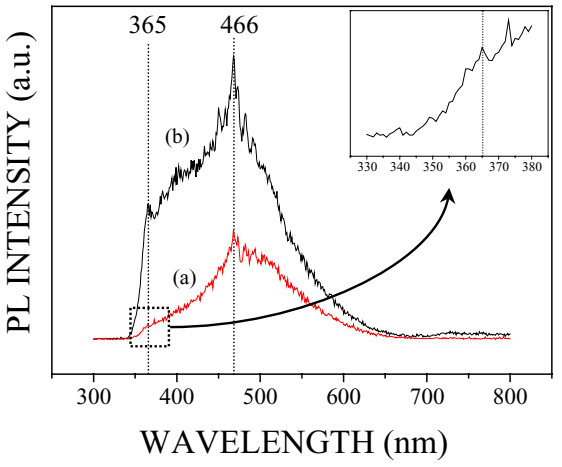


Fig. 5. PL spectra of (a) as-deposited and (b) annealed $Ga_2O_3$ films.

It is noteworthy that there is a small emission shoulder around at the energy of 3.405 eV ($\lambda = 365$ nm) for both materials and the energy belongs to the ultraviolet (UV) region. UV luminescence has been reported to be attributed to an intrinsic transition, due to the recombination of a self-trapped exciton [30,31]. Since there is a similarity in the shape of measured spectra for the both films and the overall emission intensity became stronger, we surmise that the optical properties of the films are improved with the thermal annealing.

## 4. Conclusion

In summary, we have deposited the $Ga_2O_3$ films on sapphire substrate using the metal organic chemical vapor deposition technique and have investigated annealing effects at a temperature of 1050 °C. The SEM images and XRD data indicate that the grained structures of β-$Ga_2O_3$ appear by the thermal annealing. The AFM analysis indicates that the rms surface roughness increases by increasing the annealing temperature. PL measurement reveals that the emission intensity in the BG and UV region becomes stronger by the thermal annealing. The first production of $Ga_2O_3$ thin films on sapphire substrates using the conventional source will shed light on their potential applications.

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