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Importance of dissolving source precursor of $Ga(C_5H_7O_2)_3$ with HCl in mist CVD for α-Ga_2O_3 growth

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Abstract

We dissolved the source precursor of $Ga(C_5H_7O_2)_3$ with either hydrochloric acid (HCl) or nitric acid (HNO_3) in the mist chemical vapor deposition (mist CVD) growth of α-Ga_2O_3 films on α-Al_2O_3 substrates. Enough film thickness was obtained when HCl was used as a source solvent, while less growth occurred when HNO_3 was used. With the increase of HCl concentration, it was observed that the film thickness as well as grain size tended to increase. These results indicate that chloride ion plays an important role in the mist CVD growth of α-Ga_2O_3.

1. Introduction

Recently, gallium oxide (Ga_2O_3) has been attracting attention as a next primary material suitable for power electronics, deep ultraviolet detectors, etc [1]. Ga_2O_3 has six polymorphs (α, β, γ, δ, ε, and κ). Although the monoclinic β-Ga_2O_3 is the most thermodynamically stable phase, we have focused on the metastable α-Ga_2O_3 by virtue of the following advantages. The bandgap energy is 5.3-5.6 eV, which is the largest among the polymorphs [2]. Since some of the oxides have a corundum structure such as α-Al_2O_3 and α-In_2O_3, bandgap engineering is possible by alloying with these materials. The growth of high quality α-Ga_2O_3 film is possible by the novel crystal growth technology of mist chemical vapor deposition (mist CVD) growth method [3].

Mist CVD is a growth technique working at atmospheric pressure. This method does not require a vacuum environment, making the system configuration simple and inexpensive. Mist is generated by ultrasonic transducer to atomize source solution and it is transferred to growth furnace by a carrier gas. Against the accomplishments of successful growth of high quality α-Ga_2O_3 by Mist CVD method, the growth mechanism has not fully clarified yet. We have been using a small amount of HCl to enhance dissolution of source precursor. In the previous report [4], HCl was found to affect growth rate, purity, and surface roughness in the mist CVD growth of α-Ga_2O_3. Further study is necessary to understand the role of HCl in the mist CVD growth of α-Ga_2O_3.

In this study, we dissolved the source precursor of $Ga(C_5H_7O_2)_3$ with either HCl or HNO_3 in the mist CVD growth of α-Ga_2O_3 films on α-Al_2O_3 substrates. The impact of HCl as a source solvent was investigated.

2. Experiment

The α-Ga_2O_3 thin films were grown by mist CVD for 1h on (0001) α-Al_2O_3 substrates with off-cut angles of 0.2° to the m-axis. $Ga(C_5H_7O_2)_3$ was used as a source precursor. The precursor was first dissolved in deionized water to prepare a solution with precursor concentration of 0.05 mol/L, then 36% HCl and 60% HNO_3 aqueous solutions were added so as to vary the concentration from 0.10 mol/L to 0.47 mol/L. The growth temperature was 460°C. The precursor solution was atomized by an ultrasonic transducer with a frequency of 2.4 MHz, and the aerosol was transferred to the substrate using oxygen carrier gas.

The crystal structure was determined by X-ray diffraction (XRD). Film thickness was evaluated by scanning electron microscopy (SEM) and spectroscopic ellipsometry (SE). Surface morphology was evaluated by atomic force microscopy (AFM).

3. Results and Discussion

Figure 1 shows representative XRD θ-2θ profiles for the films grown using either HCl or HNO_3 with a concentration of 0.10 mol/L. The 0006 diffraction peak of the α-phase Ga_2O_3 was dominantly observed for both films. The 0004 peak of the ε-phase was occasionally observed for the films grown using HCl regardless of the concentration. Since the ε-phase has a small lattice mismatch to the α-Al_2O_3 [5], ε-phase is considered to be easily formed. Full width at half maximum values of the X-ray rocking curve (XRC) 0006 diffraction peaks of the α-phase Ga_2O_3 shown in Fig. 1 were 32 and 309 arcsec. for films grown using either HCl and HNO_3, respectively. This can be attributed to the difference in the film thicknesses; 500 and 40 nm for the films grown using either HCl and HNO_3, respectively.

Figure 2 shows H^+ concentration dependence of the film thickness measured by cross-sectional SEM and SE. It was confirmed that the film thickness increased with increasing the HCl concentration and mostly saturated at about 1500 nm. On the other hand, less growth occurred when HNO_3 was used. Both HCl and HNO_3 are strong acids. Therefore, chloride ion is considered to play an important role in the mist CVD growth of α-Ga_2O_3.

AFM images of the α-Ga_2O_3 films grown using HCl varied between 0.10 and 0.47 mol/L are summarized in Fig. 3. All the films exhibited granular surface morphology. It must be emphasized that grain size became larger with the increase in HCl concentration. This result agrees with the previous report [4] and this would also assist that chloride ion is considered to play an important role in the mist CVD growth of α-Ga_2O_3.

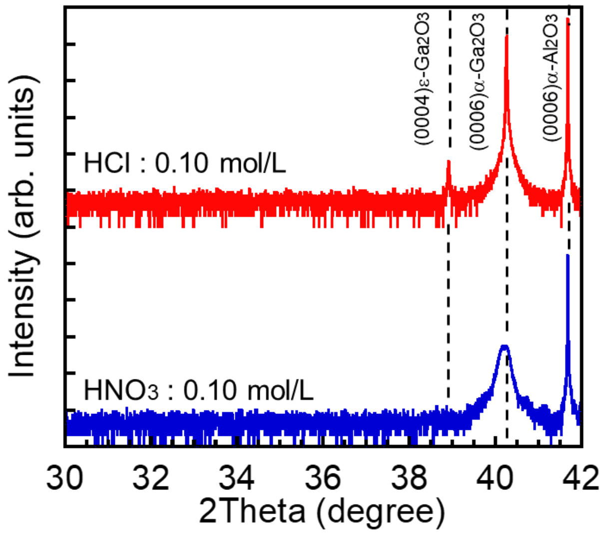

Fig.1 XRD θ-2θ profiles of Ga_2O_3 films grown using either HCl or HNO_3 with concentration of 0.10 mol/L in the source solution.

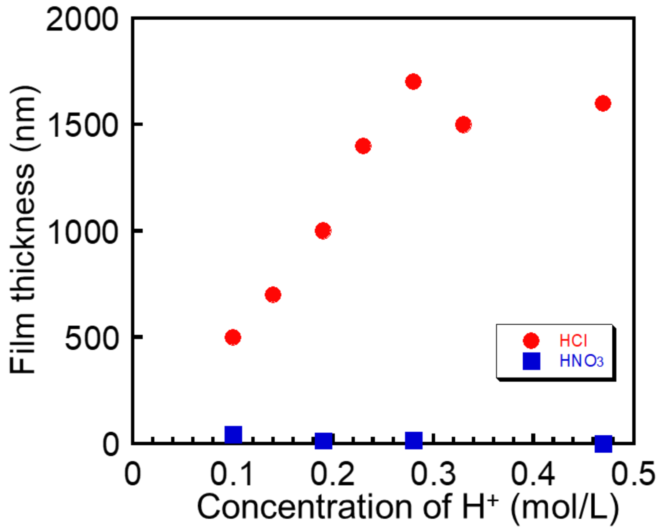

Fig. 2 Thickness of α-Ga_2O_3 films as functions of HCl and HNO_3 concentration. HCl and HNO_3 concentrations were varied from 0.10 mol/L to 0.47 mol/L at growth temperature of 460°C.

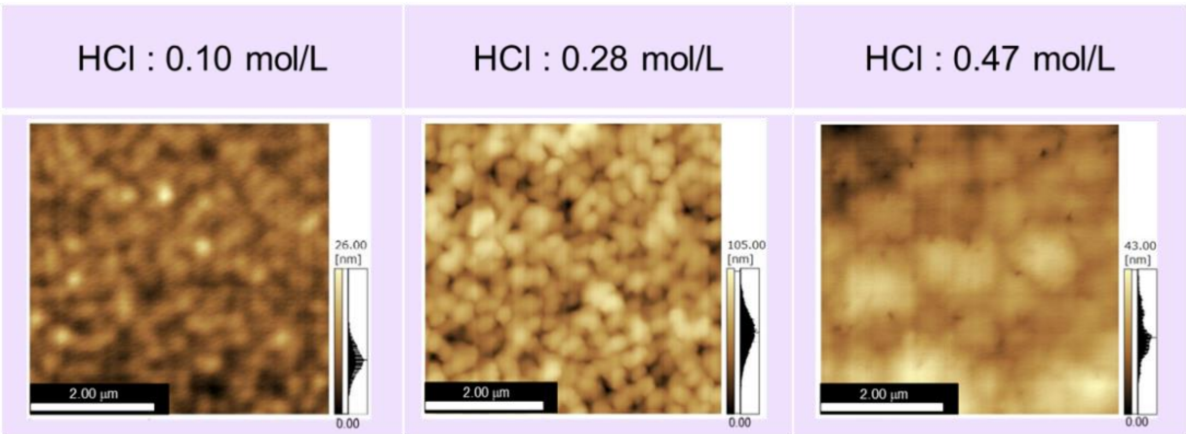

Fig. 3 AFM images of α-Ga_2O_3 films grown using HCl with concentrations of 0.10, 0.28, and 0.47 mol/L.

4. Conclusions

We dissolved the source precursor of $Ga(C_5H_7O_2)_3$ with either HCl or HNO_3 in the mist CVD growth of α-Ga_2O_3 films on α-Al_2O_3 substrates. α-Ga_2O_3 was dominantly grown both using HCl and HNO_3. It was confirmed from cross-sectional SEM and SE measurements that the film thickness increased with increasing the HCl concentration and mostly saturated at about 1500 nm. On the other hand, less growth occurred when HNO_3 was used. It was also confirmed from AFM measurement that the growth using HCl films exhibited granular surface morphology. The grain size became larger with the increase of HCl concentration. These results indicate that chloride ion is considered to play an important role in the mist CVD growth of α-Ga_2O_3.

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