Chemical Vapor Deposition of Ga_2O_3 Thin Films on Si Substrates

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Amorphous Ga_2O_3 films have been grown on Si(100) substrates by metal organic chemical vapor deposition (MOCVD) using gallium isopropoxide, $Ga(O^iPr)_3$, as single precursor. Deposition was carried out in the substrate temperature range 400-800 °C. X-ray photoelectron spectroscopy (XPS) analysis revealed deposition of stoichiometric Ga_2O_3 thin films at 500-600 °C. XPS depth profiling by Ar^+ ion sputtering indicated that carbon contamination exists mostly in the surface region with less than 3.5% content in the film. Microscopic images of the films by scanning electron microscopy (SEM) and atomic force microscopy (AFM) showed formation of grains of approximately 20-40 nm in size on the film surfaces. The root-mean-square surface roughness from an AFM image was ~10 Å. The interfacial layer of the Ga_2O_3/Si was measured to be ~35 Å thick by cross-sectional transmission electron microscopy (TEM). From the analysis of gaseous products of the CVD reaction by gas chromatography-mass spectrometry (GC-MS), an effort was made to explain the CVD mechanism.

Keywords : Gallium oxide, Metal organic chemical vapor deposition, Single precursor, Gallium isopropoxide.

Introduction

Thin films of metal oxides are finding rapidly growing applications in advanced materials technologies. The metal oxides exist in a variety of compositions and crystal structures, and their properties vary widely, from insulators to superconductors, leading to a vast range of potential applications. Gallium oxide films have recently attracted attention due to their applications as dielectric films on GaAs substrates in metal-oxide-semiconductor field-effect transistors, phosphor host materials in emissive displays, and also oxygen and reducing gas sensors, etc.[1-6]

The gallium oxide films have been mainly grown on Al_2O_3 and GaAs substrates by physical deposition methods such as evaporation or sputter deposition.[7-11] Metal organic chemical vapor deposition (MOCVD) employed in this study offers most flexible approach to the growth of metal oxides. In addition, this method can offer several advantages: good step coverage, producing uniform, pure, reproducible, and adherent films.[12,13] An essential requirement of the MOCVD technique is the availability of suitable precursors with sufficient volatility and stability, as well as adequate purity. In spite of the their applicable interests and several advantages of CVD process, only a few studies have been reported on the growth of gallium oxide films by CVD.[14-17] For the CVD growth of gallium oxide thin films, $Ga(hfac)_3$ with O_2[14,15] and $Ga[OCH(CF_3)_2]_3 \cdot HNMe_2$ with moist air[16] were used as precursors. To our knowledge, only one study[17] was reported on the Ga_2O_3 thin film growth on the Si substrate by CVD, using $[Ga(\mu\text{-O-}t\text{-Bu})(O\text{-}t\text{-Bu})_2]_2$ with and without oxygen. Although Al_2O_3 and GaAs have been widely used for the growth of Ga_2O_3 thin films, Si is one of the most promising substrates for the semiconductor device technology. In particular, using a single CVD source provides a novel alternative to conventional CVD that employs separate sources for the constituent elements of compound materials.

In this paper, we report on the growth of amorphous Ga_2O_3 thin films on Si substrates by CVD using gallium isopropoxide, $Ga(O^iPr)_3$, which is rather a simple compound, as single source having a ready-made bonding between Ga and O without any extra oxygen source or carrier gas. The as-grown Ga_2O_3 thin films were characterized by several analysis techniques. The chemical composition of the films was determined by X-ray photoelectron spectroscopy (XPS). The morphology and surface roughness of the films were examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. The Ga_2O_3/Si interfacial region was examined by cross-sectional transmission electron microscopy (TEM). Gaseous products of the CVD reaction were analyzed by gas chromatography-mass spectrometry (GC-MS) in order to elucidate the CVD mechanism.

Experimental Section

The Ga_2O_3 thin films were grown in a high vacuum CVD chamber, the base pressure of which was ~1×10^{-7} Torr. The precursor, $Ga(O^iPr)_3$, was purchased from Kojundo Chemical Laboratory Co., Ltd. Si(001) wafers (p-type, $7 \times 15 \times 0.6$ mm^3) were used as substrate. In order to form a hydrogen-terminated surface on a substrate prior to its introduction into the chamber, it was treated by the well-known wet chemical process, *i.e.*, degreasing in deionized water and acetone, boiling in a solution of $H_2SO_4 : H_2O_2 =$

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2 : 1 and subsequent etching in 10% HF and rinsing in deionized water. Then, the H-terminated substrate was loaded in the reaction chamber. Prior to growth, the substrate was resistively heated to 800 °C to remove the hydrogen adlayer. The substrate temperature was monitored by an infrared optical pyrometer. Deposition was carried out under the following conditions: The substrate was heated to the growth temperature in the range 400-800 °C for deposition. The precursor $Ga(O^iPr)_3$ was heated at 90-100 °C. It can be synthesized from the reaction of $Ga(OEt)_3$ and isopropanol by alcohol interchange reaction and has the vapor pressure of 0.15 Torr at 109.5 °C.[18] The deposition lasted 8 h under the growth pressure of 5×10^{-5} Torr.

Results and Discussion

In all temperature ranges, as-grown gallium oxide films had an amorphous phase, confirmed by XRD. The films appeared smooth and well adherent to the substrates.

Firstly, XPS analysis was performed to determine the composition of gallium oxide films formed at the substrate temperature of 400-800 °C. For the films grown at 400-500 °C, the normalized intensity ratio of the Ga 2p peak to O 1s peak calculated by the integrated intensities and the photoionization cross-sections showed the tendency of formation of gallium-rich films (Ga : O ≈ 1.0 : 1.0). In the temperature range 500-600 °C, stoichiometric Ga_2O_3 films were mostly obtained. Above ~700 °C, the films did not grow well. Figure 1 shows a typical X-ray photoelectron survey spectrum of a Ga_2O_3 film grown at ~600 °C for 8 h. The spectrum displays both the photoelectron and Auger electron peaks for gallium and oxygen with carbon contamination. From this spectrum, the ratio Ga : O is estimated to be about 1 : 1.6. The carbon contamination, after Ar^+ ion sputtering (1 keV, 20 min), was considerably reduced, below 3.5%. It indicates that the carbon contamination exists mostly in the surface region of the film and does not exist in the bulk of the film. In the inset of Figure 1, the high-resolution Ga 3d core level spectrum is shown with the curve-fitted results. The binding energy of the Ga 3d core level is ~21.1 eV. The binding energy positions of the Ga 3d as well as Ga $2p_{3/2}$ (1118.5 eV) and O 1s (531.5 eV) core levels are well consistent with previous XPS studies.[17,19,20] Further, small and broad tail at a higher energy side of the main peak (at ~24 eV) is possibly due to the presence of the contribution from the oxygen 2s core level.[21] From the XPS result, it is found that stoichiometric Ga_2O_3 films are properly formed at substrate temperatures of 500-600 °C. Similar amorphous Ga_2O_3 thin films were obtained in previous CVD studies: using $Ga(hfac)_3$ at substrate temperatures of 400-500 °C with O_2,[14,15] using $Ga[OCH(CF_3)_2]_3 \cdot HNMe_2$ with moist air at 250-450 °C,[16] as well as using $[Ga(\mu\text{-O-}t\text{-Bu})(O\text{-}t\text{-Bu})_2]_2$ with and without O_2 at 300-700 °C.[17]

Microscopic examinations were then carried out for a Ga_2O_3 film grown at 600 °C. Figure 2 shows the plan-view (a) and cross-sectional (b) SEM images of the Ga_2O_3 film. The Ga_2O_3 film shows a relatively smooth and two-dimensional surface without any cracks or pits on the surface. The surface shows many small lateral grains having the average size of some tens of nanometers. The cross-sectional SEM image shows an abrupt and flat interface between the Si substrate and the Ga_2O_3 film. The thickness of the film is ~0.35 μm, indicating a growth rate of ~7.3 Å/min. Interestingly, this growth rate is much similar to that of the CVD result obtained using $[Ga(\mu\text{-O-}t\text{-Bu})(O\text{-}t\text{-Bu})_2]_2$ without oxygen.[17]

In order to get a more detailed microscopic image for

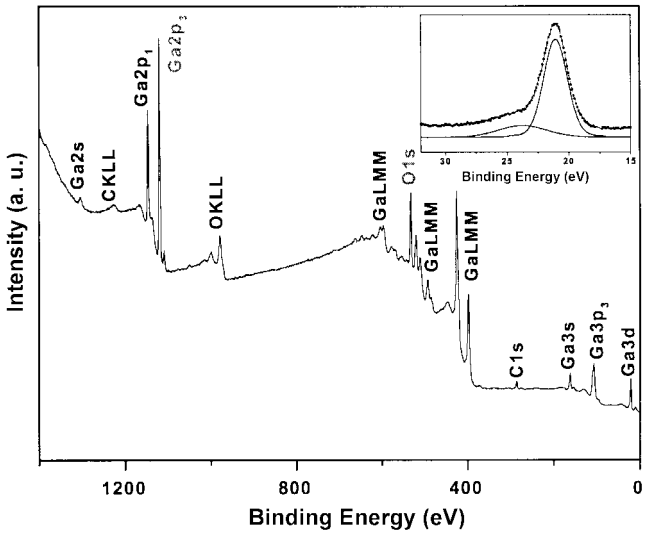

Figure 1. X-ray photoelectron survey spectrum of the gallium oxide thin film deposited at the substrate temperature of ~600 °C for 8 h. In the inset, the Ga 3d core level spectrum is shown with the curve-fitted results.

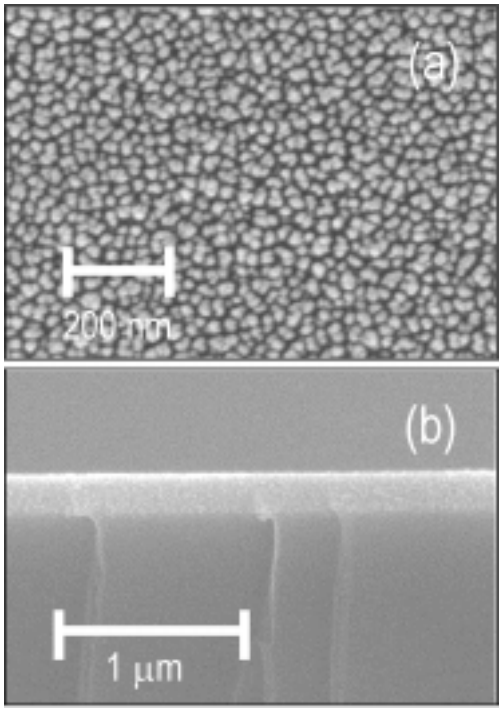

Figure 2. Plan-view (a) and cross-sectional (b) SEM images of the Ga_2O_3 film of Figure 1.

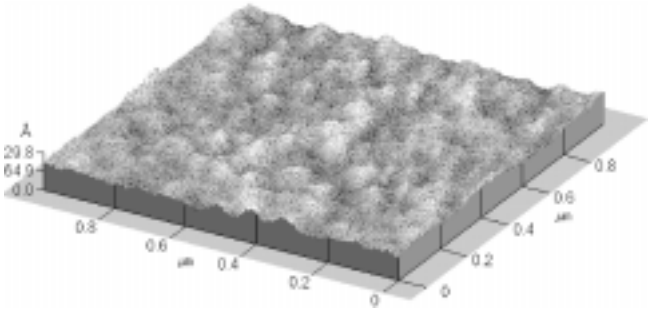

Figure 3. An AFM image of the Ga_2O_3 film grown at 600 °C. The image was obtained over the area of 1×1 μm^2 in a non-contact mode.

surface roughness, an AFM image was also taken over the area of 1×1 μm^2 in a non-contact mode as shown in Figure 3. The root mean square (RMS) roughness of the Ga_2O_3 thin film was found to be ~10 Å, which indicates the flatness of the film.

Figure 4 shows the TEM image of the interfacial region between the Ga_2O_3 film and the Si substrate. The interface between the Ga_2O_3 film and the Si substrate is clearly distinguished although there exists a ~35 Å thick, dark interfacial layer on the side of the Ga_2O_3 film. A closer examination of the magnified TEM image of this layer confirms that it is not a mixed layer of silicon and gallium oxide. The grains in this region are not distinguishable from those of the bulk of the film, therefore, it is probably due to contrast difference arising from subtle differences in the density of the Ga_2O_3 film at the interface and in the bulk.

Finally, the gaseous products of the CVD reaction were analyzed by GC-MS to elucidate the CVD mechanism. After the thermal decomposition of the precursor, the gaseous products were found to consist mainly of propylene (51.8%), 2-propanol (19.3%), and acetone (21.7%). Thus, it is proposed that, for the heterogeneous pyrolysis of $Ga(O^iPr)_3$ on silicon, the CVD mechanism can be partly explained as suggested in Figure 5. A molecule of $Ga(O^iPr)_3$ first produces a hydrogallium diisopropoxide molecule releasing one molecule of acetone by β-hydride (β-positioned hydrogen from the

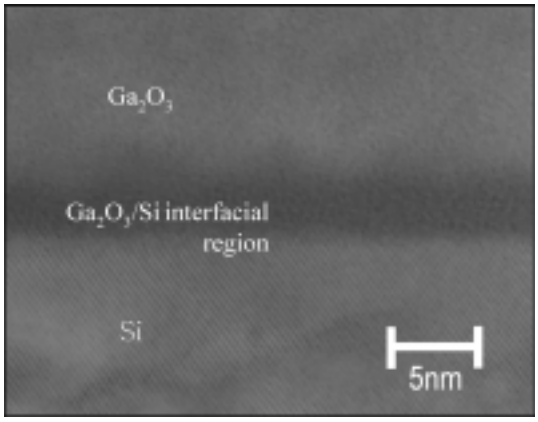

Figure 4. A cross-sectional TEM image of the Ga_2O_3 film grown at 600 °C.

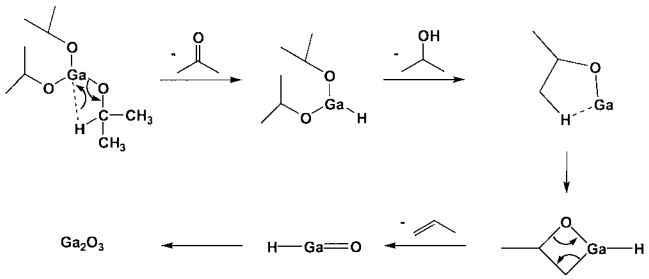

Figure 5. A proposed mechanism of the Ga_2O_3 CVD using $Ga(O^iPr)_3$ as precursor.

gallium atom) elimination of an isopropoxide ligand. The resulting hydrogallium diisopropoxide goes through a reductive coupling reaction between an isopropoxide ligand and a hydride to afford gallium monoisopropoxide and isopropyl alcohol. A γ-hydride of the isopropoxide ligand in gallium monoisopropoxide can then be activated through γ-hydride elimination to make a hydrometallacyclobutane ring which undergoes the reaction to give rise to hydrogallium oxide and propylene. Hydrogallium oxide might be finally decomposed to gallium oxide and hydrogen gas, however, the evolution of hydrogen was not examined in this experiment. This scheme cannot be fully proven at this stage, but given the gaseous products of the CVD reaction as above, it can be a possible explanation of the CVD mechanism.

Summary

Amorphous Ga_2O_3 thin films have been grown on Si(100) substrates by MOCVD at the temperature range 400-800 °C using gallium isopropoxide, $Ga(O^iPr)_3$, as single precursor. Stoichiometric Ga_2O_3 thin films were grown at 500-600 °C and characterized by XPS. By SEM and AFM images, it was found that the Ga_2O_3 film grown at 600 °C for 8 h has smooth surface morphology and a flat surface. The RMS surface roughness was ~10 Å. A cross-sectional TEM image shows that the Ga_2O_3 film is amorphous and the interface between the Si substrate and the Ga_2O_3 film is sharp although a dark interfacial layer of ~35 Å thick exists on the side of the film. GC-MS analysis of the pyrolysis products of the precursor, $Ga(O^iPr)_3$, indicates as a way of explanation that the precursor is thermally decomposed through β-hydride elimination reaction, reductive coupling reaction, and γ-hydride elimination reaction to produce acetone, isopropyl alcohol, and propylene with Ga_2O_3.

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