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MOCVD Growth and Annealing of Gallium Oxide Thin Film and its Structural Characterization

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Abstract. We have demonstrated the production of gallium oxide thin films on various substrates such as Si(111), SiO_2, and sapphire by metalorganic chemical vapor deposition using the trimethylgallium (TMGa) as a precursor in the presence of oxygen. The XRD data revealed that the as-deposited gallium oxide films were fully amorphous but very small crystallites with monoclinic structures were found with the thermal annealing at a sufficiently high temperature, regardless of substrate materials. The AFM analysis indicated that the surface roughness increased by the thermal annealing.

Introduction

Gallium oxide has recently attracted interests as a new material for gas sensor [1,2], transparent conductor [3], phosphor [4,5], and solar cells [6,7]. For the production of gallium oxide films, various synthetic methods such as oxidation of Ga-containing surfaces [8-10], sol-gel process [11], sputtering [12-14], pulsed laser deposition [15], molecular beam epitaxy [16], and chemical vapor deposition (CVD) have been studied. In order to use the metal organic CVD method [17,18], which has an advantage of good step coverage, uniformity and reproducibility, the precursors of $Ga(hfac)_3$ with O_2 [8], $Ga[OCH(CF_3)_2]_3 \cdot HNMe_2$ with H_2O [19], and $[Ga(\mu\text{-O-t-Bu})(\text{O-t-Bu})_2]_2$ with O_2 [20] have been developed.

Although we have reported the preparation of gallium oxide thin films on sapphire substrates, in this paper [21], we investigate the growth behaviors of gallium oxide films on various substrates such as Si, SiO_2, and sapphire, using a simple reaction of a trimethylgallium (TMGa) and oxygen (O_2) mixture at a temperature of 550 ℃. We also investigate the effect of thermal annealing at a temperature of 1050℃ on the structural property of thin films.

Experiments

The Si substrate was p-type with (111) orientation. The Si substrate was cleaned in acetone for 10 min, HF (20:1) for 10 sec, and then rinsed in deionized water for 1 min before loading into the MOCVD sysstem. The SiO_2 substrates were produced by thermally growing a 60 nm-thick SiO_2 layer on the Si substrate. The sapphire substrate was (0001)-oriented. A schematic diagram of the MOCVD reactor used in our experiments was previously described [22].

High-purity Ar (99.999% purity) passed through the TMGa bubbler and delivered TMGa vapor to the reactor. The TMGa bubbler was maintained at the temperature of -5 ℃. The film was synthesized by supplying O_2 and Ar carrier gases with the flow rate of 30 sccm and 30 sccm, respectively in the temperature range of 550 ℃ for 10 minutes. After the deposition of films, samples were annealed in a quartz tube furnace at a temperature of 1050℃ for 60 minutes in air ambient.

A scanning electron microscopy (SEM: Hitachi S-4200, 30 kV) was used to observe the structure morphology of gallium oxide film and an x-ray diffraction (XRD: Philips, CM20T, 200 kV, CuKa1

λ =1.5405 Å) was used to characterize the structural quality of the films. An atomic force microscopy (AFM: Nanoscope III, Digital Instruments) was used to evaluate the surface roughness of the films.

Results and discussion

Fig. 2a, 2b, and 2c show the SEM images of gallium oxide thin films, respectively, which are deposited on Si(111), SiO_2, and sapphire substrates. On the other hand, Fig. 2d, 2e, and 2f show the SEM images of gallium oxide thin films, which are annealed at a temperature of 1050℃, respectively, deposited on Si(111), SiO_2, and sapphire substrates. Plan-view SEM images indicate that by the thermal annealing process at 1050℃, the microstructure tends to change into the grain-like structures, regardless of substrate material. The cross-sectional SEM images also indicate that although no clear grain boundaries are found inside the as-grown gallium oxide thin films, the grain-like structure appears by the thermal annealing.

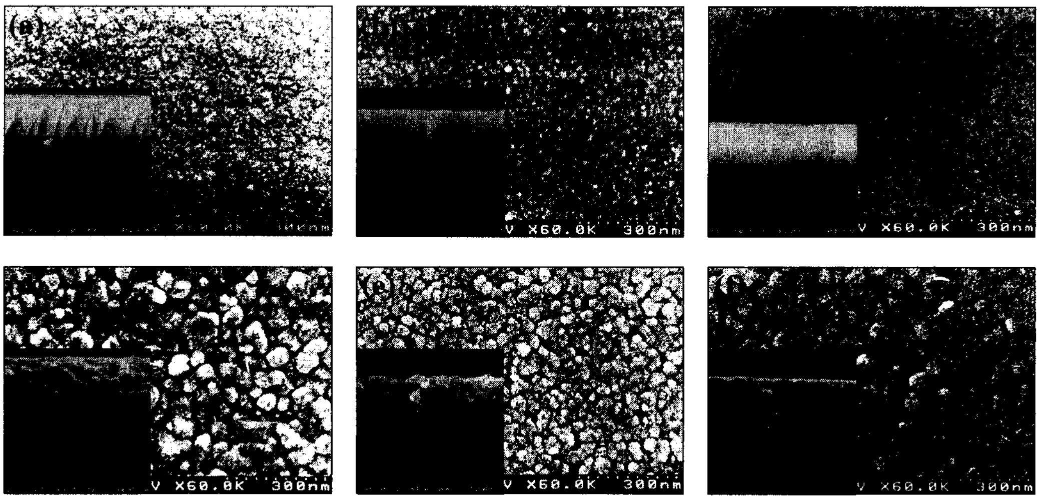

Fig. 1. Plan-view SEM images (Inset: cross-sectional SEM images) of (a,b,c) as deposited and (d,e,f) 1050℃-annealed gallium oxide thin films on (a,d) Si(111), (b,e) SiO_2, and (c,f) sapphire substrates.

In order to investigate the surface roughness of the as-frown and annealed gallium oxide films, we have performed an AFM analysis. Fig. 2a, 2b, and 2c show the AFM topographies representing the surface morphology of gallium oxide thin films, respectively, which are deposited on Si(111), SiO_2, and sapphire substrates. On the other hand, Fig. 2d, 2e, and 2f show the AFM topographies representing the surface morphology of gallium oxide thin films, which are annealed at a temperature of 1050℃, respectively, deposited on Si(111), SiO_2, and sapphire substrates. The grain-like structures are clearly observed on top of the gallium oxide film after the thermal annealing, regardless of the substrate material. The root-mean-square (RMS) surface roughnesses of the as-deposited and 1050℃ -annealed gallium oxide films on Si(111), SiO_2, and sapphire substrates, respectively, are 1.09 nm and 4.01 nm, 0.89 nm and 3.56 nm, and 1.15 nm and 2.28 nm, indicating that the surface of annealed gallium oxide film is rougher than that of the as-deposited film. We surmise that the surface becomes rougher due to the appearance of grains on top of the films, and thus the AFM images agree with the plan-view SEM images.

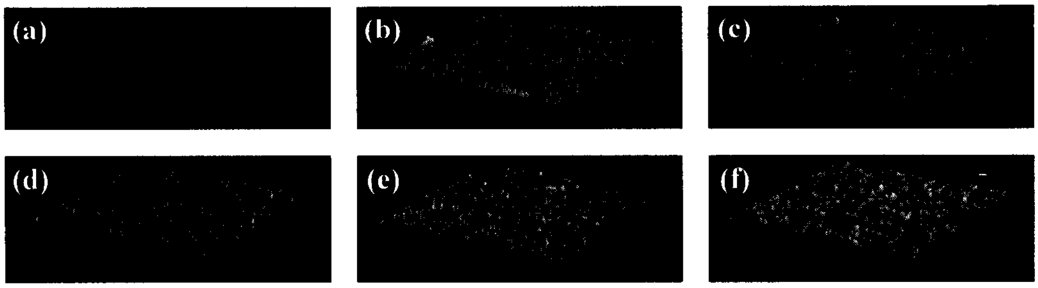

Fig. 2. AFM images representing the surface morphology of (a,b,c) as deposited and (d,e,f) 1050℃ -annealed gallium oxide thin films on (a,d) Si(111), (b,e) SiO_2, and (c,f) sapphire substrates.

In order to investigate the effect of thermal annealing on the crystallinity of gallium oxide thin film, we have performed an XRD analysis on the as-deposited and 1050℃-annealed samples. Fig. 3a, 3b, and 3c show the XRD diffraction pattern of gallium oxide thin films, respectively, which are deposited on Si(111), SiO_2, and sapphire substrates. Due to the absence of a distingushiable Ga_2O_3 diffraction peak from the as-deposited samples, we suppose that the gallium oxide films have a fully amorphous structure, regardless of the substrate material. On the other hand, Fig. 3d, 3e, and 3f show the XRD diffraction pattern of gallium oxide thin films, which are annealed at a temperature of 1050 ℃, deposited on Si(111), SiO_2, and sapphire substrates, respectively, indicating that the lines observed in the diffractograms are found to coincide with (004), $(\bar{2}02)$, (111), $(\bar{1}13)$, $(\bar{2}17)$, and (311) peaks of monoclinic β-Ga_2O_3 obtained from the Joint Committee on Powder Diffraction Standards (JCPDS) card (No. 11-370). The stable β-Ga_2O_3 phase is known to have a monoclinic structure. The existence of the β-Ga_2O_3 peaks indicates the production of the monoclinic Ga_2O_3 crystallites by the thermal annealing at a sufficiently high temperature.

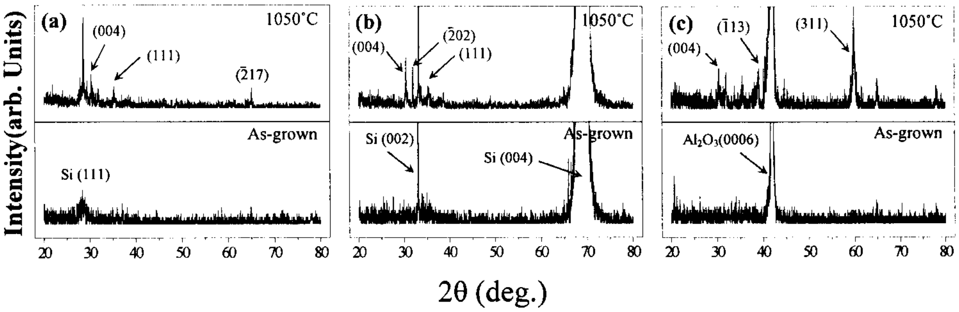

Fig. 3. XRD patterns of as deposited and 1050℃-annealed gallium oxide thin films on (a) Si(111), (b) SiO_2, and (c) sapphire substrates.

Summary

We have prepared the gallium oxide films on Si(111), SiO_2,and sapphire substrates by a reaction of a TMGa and O_2 mixture and have investigated the effects of postdeposition annealing. The SEM images indicate that grain-like structures appears by the thermal annealing and the AFM images reveals that the RMS surface roughness increase by the thermal annealing, regardless of substrate material. The XRD data indicate that even though the as-deposited gallium oxide films turns out to be fully amorphous, the β-Ga_2O_3 phases appear by the thermal annealing. The production of gallium oxide thin films on various substrates using the conventional source and the possibility of crystallization by thermal annealing will shed light on the potential application of Ga_2O_3 films.

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