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Thermal Stability of α-$(Al_xGa_{1-x})_2O_3$ Films Grown on C-Plane Sapphire Substrates

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Abstract

Thermal stability of α-$(Al_xGa_{1-x})_2O_3$ ($0 \leq x \leq 0.9$) films grown on c-plane sapphire substrates was investigated. The α-$(Al_xGa_{1-x})_2O_3$ epitaxial films were annealed at the temperatures in the range of 600-1000 °C in air and then investigated by X-ray diffraction and transmission electron microscopy. When the Al composition is smaller than 0.5, the annealing process converted the α-$(Al_xGa_{1-x})_2O_3$ films to the β-phase, which is the thermodynamically most stable phase for Ga_2O_3. On the other hand, for $0.65 \leq x < 0.9$, α-$(Al_xGa_{1-x})_2O_3$ did not show the phase transition to the β-phase upon high temperature annealing. These results agree well with a theoretical phase diagram.

1. Introduction

α-$(Al_xGa_{1-x})_2O_3$ alloys in the trigonal corundum structure (α-phase) have been attracting much interest as materials for heterostructure electronic and photonic devices due to their large bandgaps spanning ~5.3 to 8.8 eV [1,2]. The α-phase is the thermodynamically most stable phase of Al_2O_3, while α-Ga_2O_3 is metastable since Ga_2O_3 adopts the monoclinic β-gallia structure (β-phase) as the most stable structure. The theoretical study using hybrid density functional theory calculations elucidated that the β-phase is the preferred structure up to 71% Al concentration [3]. Although α-$(Al_xGa_{1-x})_2O_3$ can be stabilized on sapphire in the entire range of Al contents [1,4], α-$(Al_xGa_{1-x})_2O_3$ films ($x \leq 0.7$) has been experimentally reported to convert to the β-phase upon heating at atmospheric pressure at 600-950 °C [5]. On the other hand, the phase stability of Al-rich α-$(Al_xGa_{1-x})_2O_3$ has not been studied in detail. Al-rich α-$(Al_xGa_{1-x})_2O_3$ holds the key to achieve α-$(Al_xGa_{1-x})_2O_3$ based devices at bandgaps beyond the reach of all other semiconductor materials, thus it is important to reveal the phase stability of α-$(Al_xGa_{1-x})_2O_3$ with high Al contents. In this study, we investigate the phase stability of α-$(Al_xGa_{1-x})_2O_3$ films grown on c-plane sapphire substrates up to $x \sim 0.9$.

2. Experimental Methods

α-$(Al_xGa_{1-x})_2O_3$ films were grown on c-plane sapphire substrates at 700 ºC using a hot-wall type mist-CVD system. Gallium (III) acetylacetonate [Ga(acac)$_3$] and aluminum (III) acetylacetonate [Al(acac)$_3$] were used as gallium and aluminum precursors, respectively. The α-$(Al_xGa_{1-x})_2O_3$ alloys were prepared by dissolving the source materials of Ga and Al together in deionized water and the alloy composition was controlled by changing the molar ratios of Ga to Al in the source solution. The α-$(Al_xGa_{1-x})_2O_3$ films were post-annealed in an atmospheric furnace for 30 min at annealing temperatures (T_A) after the growth. The phase stability of the α-$(Al_xGa_{1-x})_2O_3$ films against the thermal treatment was investigated by symmetric X-ray diffraction (XRD) 2θ/ω measurements using monochromatic Cu Kα_1 radiation (λ=1.54056 Å) at room temperature for the samples after annealing. The Al composition in the films were estimated, assuming Vegard's law from diffraction peak positions of the XRD scan profiles for the samples.

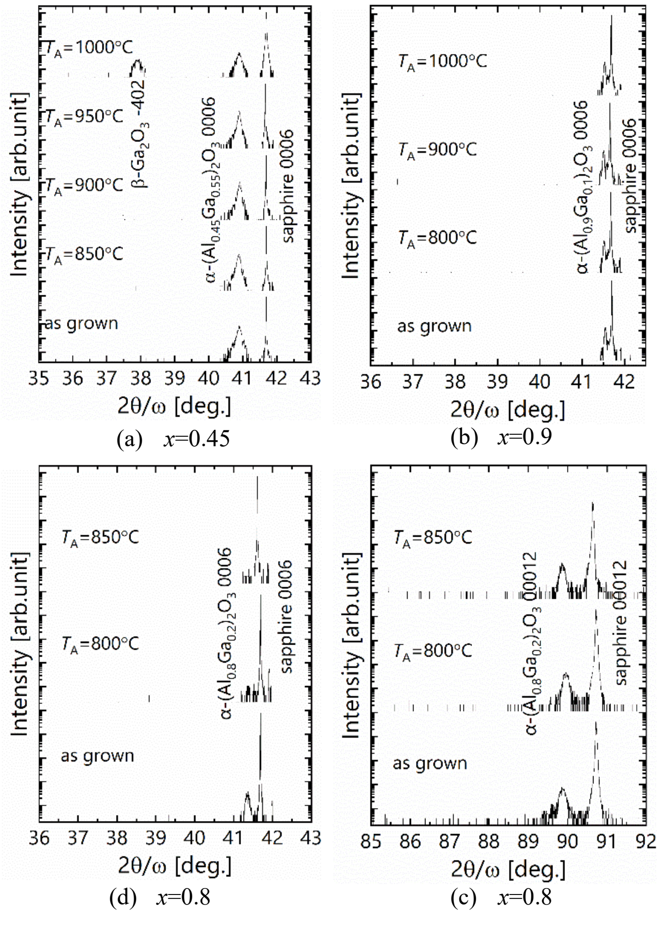

Fig. 1. XRD 2θ/ω scan profiles for the α-$(Al_xGa_{1-x})_2O_3$ films before and after annealing at T_A for (a) x=0.45, (b) x=0.9 and (c) x=0.8. (d) higher angle range for x=0.8.

3. Results and Discussion

The XRD 2θ/ω profiles revealed that, for x≤0.45, the phase transformation of the α-(Al_xGa_{1-x})$_2O_3$ films to the β-phase occurred after the thermal treatment. We prepared the α-(Al_xGa_{1-x})$_2O_3$ films with different film thicknesses, but the significant dependence of the phase transition temperature on the thickness was not observed in the range below 200 nm. The temperature of the phase transition increased with Al concentration up to 0.45 and the α-(Al_xGa_{1-x})$_2O_3$ film (x=0.45) maintained the corundum structure after annealing at T_A=950 °C. On the other hand, for x≥0.65, the phase transition to the β-phase was not detected from the XRD measurements. The film with x= 0.9 remained the α-phase at the annealing temperature up to 1000 °C. These results agree well with the theoretical result that the α-phase is energetically preferable for the higher Al content than 0.71 [3]. However, for x=0.65 and 0.8, the intensity of diffraction peaks originated from α-(Al_xGa_{1-x})$_2O_3$ 0006 decreased after annealing at 800 °C, while peaks from α-(Al_xGa_{1-x})$_2O_3$ 00012 remained with the same intensities as those of the as grown samples.

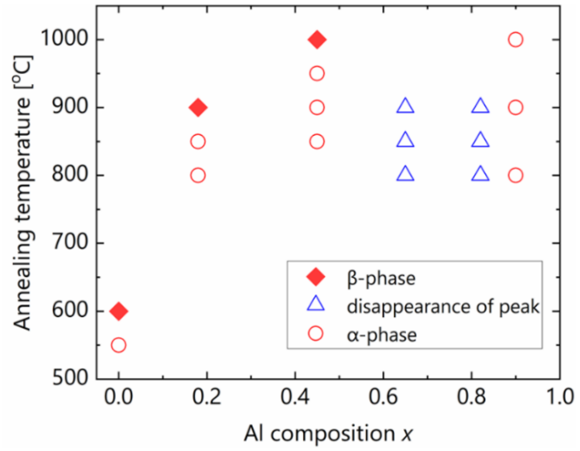

Fig.2. Phase stability of the α-(Al_xGa_{1-x})$_2O_3$ films as a function of x. Red solid rhombs, blue open triangles and red open circles show the samples which converted to the β-phase, those whose intensity of 0006 diffraction peaks decreased and those which maintained the α-phase at the annealing temperatures.

In order to discuss the crystal structure of the sample which showed the disappearance of the 0006 reflex of the XRD profile, we observed the cross-sectional transmission electron microscopy (TEM) image of the α-($Al_{0.8}Ga_{0.2}$)$_2O_3$ film annealed at 850 °C. The TEM image revealed that the α-($Al_{0.8}Ga_{0.2}$)$_2O_3$ film uniformly remained on the sapphire substrate and the inclusion of the other phases was not detected as the XRD profile showed. The small regions with a darker contrast were obtained in the vicinity of the surface of the film, probably arising from the higher Ga concentration in the areas. The arrangement of the electron diffraction pattern for the α-($Al_{0.8}Ga_{0.2}$)$_2O_3$ film was same as that of the sapphire substrate, indicating that the film maintained the corundum structure after the thermal treatment. In addition, the diffraction spots elucidated the rotation of the pattern of the film by 2 degree with respect to that of the substrate. The tilting of the film may arise from misorientation and inhomogeneity of the grown films. The XRD 2θ/ω profiles were scanned along the out of plane of sapphire (0006) to which the α-($Al_{0.8}Ga_{0.2}$)$_2O_3$ (0006) was tilted by 2 degree after the thermal treatment. Therefore, the α-($Al_{0.8}Ga_{0.2}$)$_2O_3$ 0006 reflex seemed to be undetectable while the 00012 reflex, which is closer to the origin, was detectable from the XRD measurement.

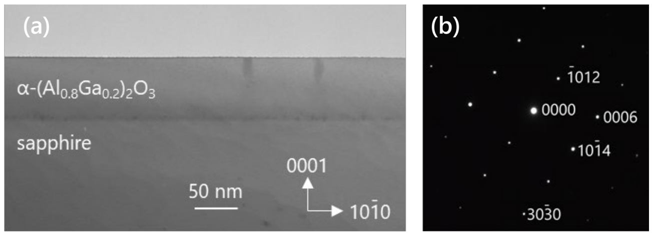

Fig.3 (a) Cross-sectional TEM image for the α-($Al_{0.8}Ga_{0.2}$)$_2O_3$/sapphire interface viewed along the <11$\bar{2}$0> zone axis. (b) Diffraction spots for the α-($Al_{0.8}Ga_{0.2}$)$_2O_3$ film.

3. Conclusions

The thermal stability of α-(Al_xGa_{1-x})$_2O_3$ epitaxial films grown on c-plane sapphire substrates was investigated by conducting thermal annealing at an atmospheric pressure. When the Al composition is lower than 0.5, the thermal stability of the α-(Al_xGa_{1-x})$_2O_3$ films was determined by the phase transition to the β-phase, enhanced by increasing the Al composition. On the other hand, for x≥0.65, the phase transformation to the β-phase was not observed after the thermal annealing up to 900-1000 °C. These results are in close agreement with theoretical phase diagrams that the α-phase is the preferred structure for the higher Al content than 0.71. The TEM observation revealed that the out of plane of the samples with x=0.8 was tilted by 2 degree after the thermal treatment, resulting in decreasing the intensity of the diffraction peak from the α-(Al_xGa_{1-x})$_2O_3$ 0006 reflex in the XRD measurement for 0.65≤x≤0.8. It is necessary to understand why the tilting of the film occurred by the annealing process in the future.

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