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Full Length Article

β-Ga_2O_3 versus ε-Ga_2O_3: Control of the crystal phase composition of gallium oxide thin film prepared by metal-organic chemical vapor deposition

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ABSTRACT

Gallium oxide thin films of β and ε phase were grown on *c*-plane sapphire using metal-organic chemical vapor deposition and the phase compositions were analyzed using X-ray diffraction. The epitaxial phase diagram was constructed as a function of the growth temperature and VI/III ratio. A low growth temperature and low VI/III ratio were beneficial for the formation of hexagonal-type ε-Ga_2O_3. Further structure analysis revealed that the epitaxial relationship between ε-Ga_2O_3 and *c*-plane sapphire is ε-Ga_2O_3 (0001) || Al_2O_3 (0001) and ε-Ga_2O_3 || Al_2O_3 . The structural evolution of the mixed-phase sample during film thickening was investigated. By reducing the growth rate, the film evolved from a mixed phase to the energetically favored ε phase. Based on these results, a Ga_2O_3 thin film with a phase-pure ε-Ga_2O_3 upper layer was successfully obtained.

1. Introduction

Gallium oxide is a wide-bandgap semiconductor that exhibits unique physical properties that are of interest for photocatalysts [1], gas sensors [2], ultraviolet photodetectors [3], and power devices [4,5]. The significant progress recently made in β-Ga_2O_3 transistors and diodes has demonstrated the great potential of Ga_2O_3 power devices for future high-power and high-voltage applications [5]. Along with the most stable β form, Ga_2O_3 has been reported to possess four additional metastable polymorphs, namely, α-, γ-, δ- and ε-Ga_2O_3 [6]. Hexagonal ε-Ga_2O_3 (space group $P6_3mc$) is considered the second-most stable phase of Ga_2O_3 [7,8]. The bandgap of ε-Ga_2O_3 has been measured to be as wide as 4.9 eV, and hexagonal ε-Ga_2O_3 is compatible with widely used hexagonal wide bandgap materials such as GaN and SiC [9,10]. Moreover, a theoretical study by Maccioni et al. suggests that ε-Ga_2O_3 would have a large spontaneous polarization and could be used to generate high-density two dimensional electron gases [8]. Their theoretical predictions were further confirmed by another study in which the ferroelectricity of ε-Ga_2O_3 was observed for the first time [11]. These unique physical properties of ε-Ga_2O_3 enable the fabrication of electronic devices using either ε-Ga_2O_3 or the combination of ε-Ga_2O_3 and other wide-bandgap materials.

Samples with high phase-purity are needed to study the properties and application of ε-Ga_2O_3. Metal-organic chemical vapor deposition (MOCVD) allows precise control of the growth rate and composition and has thus been successfully used for the deposition of high-quality compound semiconductors. Only recently, the MOCVD growth of ε-Ga_2O_3 was reported by Boschi et al. and Xia et al. [10,12] However, the growth mechanism and phase control of Ga_2O_3 remain unclear.

ε-Ga_2O_3 is metastable and will transform to the β phase between 500 °C and 870 °C [6,7,9]. Most reported MOCVD-grown Ga_2O_3 has been grown above 550 °C, which results in the β component only [13–15]. Xia et al. reported that ε-Ga_2O_3 thin films can be successfully grown on 6H-SiC at 500 °C using MOCVD [10], which indicates that decreasing the growth temperature may lead to stabilization of metastable ε-Ga_2O_3. On the other hand, the VI/III ratio is another important factor for the phase control of Ga_2O_3. A connection has been observed between the phase composition and oxygen flow rate in metal oxide thin films prepared by chemical vapor deposition [16]. However, to date, there have been no reports on the effect of the VI/III ratio on the phase composition of Ga_2O_3.

In this work, we draw a phase diagram for the MOCVD growth of Ga_2O_3 thin films with monoclinic and hexagonal structures. We demonstrate that the stabilization of metastable ε-Ga_2O_3 is primarily controlled by the growth temperature and VI/III ratio. Moreover,

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the thickness-dependent structural evolution of the mixed-phase sample is discussed in detail.

2. Experimental details

The growth of Ga_2O_3 films on *c*-plane sapphire substrates was carried out in a Emcore E400 MOCVD system. Commercially available triethyl gallium (TEGa) and high purity oxygen (O_2) were used as the precursors, and argon (Ar) was used as carrier gas. During the growth, the growth pressure was maintained at 9.1 Torr, and various growth conditions were employed to study the phase competition and transformation in the Ga_2O_3 thin films. The flow rate of TEGa and O_2 were 22.3–67.4 μmol/min and 13.4–120.5 mmol/min, respectively. The growth temperature ranged between 450 °C and 570 °C.

The film thickness was measured by a F20 Filmetrics where the Cauchy dispersion model was employed to deduce film thickness. The surface morphology was investigated using scanning electron microscopy (SEM; Hitachi S-4800). The crystal structure and phase composition were determined by X-ray diffraction (XRD) using an Empyrean X-ray diffractometer. Detailed structure analysis was performed using transmission electron microscopy (TEM; FEI Tecnai F20).

3. Results and discussion

Fig. 1 presents XRD patterns and plain-view SEM images of Ga_2O_3 thin films grown at various temperatures. During growth, the flow rate of TEGa and the VI/III ratio were kept constant at 67.4 μmol/min and 596, respectively. For growth temperatures above 535 °C, a phase-pure -oriented β-Ga_2O_3 thin film was obtained. The diffraction peaks at 18.96°, 38.38° and 59.15° are assigned to the and higher-order diffractions of β-Ga_2O_3. However, both the low intensity and large peak width of the diffraction peaks and the small grain structures observed in the SEM images (Fig. 1b and 1c) indicate the polycrystalline nature of the films. According to the XRD results, these ill-defined small grains can be identified as β-Ga_2O_3 grains.

Upon decreasing the growth temperature to 505 °C, new diffraction peaks appeared at 19.23°, 38.93°, and 59.93° (Fig. 1a). These peaks matched well with those for the crystal structure reported by Playford et al., and were indexed as 0002, 0004, and 0006 diffractions of ε-Ga_2O_3, respectively [7]. These results indicate that the Ga_2O_3 thin film transformed into a mixture of β- and ε-Ga_2O_3. Furthermore, the full-width at half-maximum (FWHM) value of the diffraction peak of β-Ga_2O_3 (0.678°) was more than three times larger than that of the ε-0006 diffraction peak (0.200°), implying that the crystal quality of ε-Ga_2O_3 was much better than that of β-Ga_2O_3 under similar growth conditions. Consistent with the XRD results, an obvious change in the surface morphology is observed in Fig. 1d. In addition to the small β-Ga_2O_3 grains, larger grains with relatively flat tops are visible. According to the XRD results, these grains can be attributed to ε-Ga_2O_3 grains with (0001) orientation. These results were further confirmed by the TEM analysis shown in Fig. 2.

Fig. 2a presents a low-magnification, cross-sectional TEM image for a thicker sample (391 nm) grown at 505 °C. Two distinct pillar-like structures are clearly identified. The dark one marked as island A has a V-shaped bottom and flat top, and the other one marked as island B is gray and hourglass-shaped. An HRTEM image of island A is presented in Fig. 2b. The lattice planes observed in Fig. 2b with interplanar distances of 0.929 and 0.252 nm correspond to ε-Ga_2O_3 (0001) and, respectively, confirming that island A is comprised of pure ε-Ga_2O_3. Comparison of the selected area electron diffraction (SAED) patterns of island A (Fig. 2e) and the sapphire substrate (Fig. 2f) further reveals the following epitaxial relationships:

$$\varepsilon - Ga_2O_3\,(0001)\,||\,Al_2O_3\,(0001)$$

$$\varepsilon - Ga_2O_3\langle 10\bar{1}0\rangle\,||\,Al_2O_3\langle 11\bar{2}0\rangle,$$

which is consistent with a study performed by Mezzadri et al. [11] The HRTEM image of island B shows that it was composed of several small β-Ga_2O_3 grains. Both 010 and 132 projections of β-Ga_2O_3 with $(\bar{2}01)$-orientation are observed (Fig. 2c), which originates from the symmetry mismatch between the monoclinic and trigonal structure [17].

The SEM and XRD results imply that the metastable ε-Ga_2O_3 tends to stabilize at lower growth temperature. However, the growth temperature window for ε-Ga_2O_3 is narrow. At 480 °C, even though grain-like structures were still observed, no diffraction peak was detectable.

Samples were also grown with different O_2 flow rates to determine the effect of the VI/III ratio. Because the XRD diffraction peaks of the β and ε phases overlap at low angles, only the portions of the XRD patterns between 2θ values of 56° and 63° are shown in Fig. 3a. For VI/III ratios above 993 at 505 °C, ε-Ga_2O_3 was no longer detected. Fig. 3a also presents the XRD patterns for samples grown under various temperature for a VI/III ratio of 1788. The phase diagram of MOCVD-grown Ga_2O_3 thin films is shown in Fig. 3b as a function of the VI/III ratio and growth temperature at a constant TEGa flow rate of 67.4 μmol/min.

The growth temperature was a crucial factor in determinining the phase composition. With decreasing growth temperature, the Ga_2O_3 films transformed from pure-β form to a mixture of β- and ε-Ga_2O_3 and finally to microcrystalline structures. The transition temperature also shifted with changing VI/III ratio. Recently, Xia et al. reported that ε-Ga_2O_3 can be successfully grown on 6H-SiC at 500 °C with a VI/III ratio as low as 390 [10]. Furthermore, Boschi et al. reported the growth of ε-Ga_2O_3 on sapphire at 650 °C using water and H_2 as the oxygen source and carrier gas, respectively [12]. In our case, a lower VI/III ratio was shown to be beneficial for the stabilization of ε-Ga_2O_3. It can further be inferred that ε-Ga_2O_3 is more stable under weakly oxidizing or even reducing atmosphere. However, reducing the VI/III ratio can only lead to a mixture of β- and ε-Ga_2O_3. Upon decreasing the VI/III ratio to ~600 at 480 °C, the film becomes microcrystalline. Single-phase ε-Ga_2O_3 could not be obtained by adjusting the growth temperature and VI/III ratio primarily because of the inevitable nucleation of β-Ga_2O_3 on the film/substrate interface, which can be attributed to the large lattice mismatch between ε-Ga_2O_3 and *c*-plane sapphire and the reaction nature of TEGa and O_2.

The structural evolution of the mixed-phase sample during the film thickening was also investigated. Three samples were grown at 505 °C with thicknesses of 34, 142 and 391 nm. XRD patterns and SEM images are presented in Fig. 4a, e, d, and c, respectively. Similar to the results in Fig. 1, small β-Ga_2O_3 grains with ill-defined shape and large ε-Ga_2O_3 grains with flat top surfaces are observed. During the initial stage of growth, β-Ga_2O_3 grains covered most of the sample surface (Fig. 4e), whereas ε-phase grains were limited. Thus, only the β- diffraction peak was detected. During the film thickening, the intensity of the β- diffraction peak continued to increase accompanied by the appearance of ε-0006 diffraction. Both the β- and ε-Ga_2O_3 grains in Fig. 4d grew into larger islands, and the surface occupancy of ε-Ga_2O_3 became nearly equal to that of β-Ga_2O_3.

Upon further increasing the film thickness to 391 nm, ε-0006 diffraction became much stronger, and the peak shifted slightly from 59.93° to 59.85°. According to Ref. [7], the ideal peak position of ε-0006 is at 59.91°, indicating that compressive strain was