Epitaxial growth of β -Ga₂O₃ thin films on Ga₂O₃ and Al₂O₃ substrates by using pulsed laser deposition

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In this work, we have successfully grown high quality epitaxial β -Ga₂O₃ thin films on β -Ga₂O₃ (100) and Al₂O₃(0001) substrates using pulsed laser deposition (PLD). By optimizing temperature and oxygen pressure, the best conditions were found to be 650–700°C and 0.5 Pa. To further improve the quality of hetero-epitaxial β -Ga₂O₃, the sapphire substrates were pretreated for atomic terraced surface by chemical cleaning and high temperature annealing. From the optical transmittance measurements, the films grown at 600–750°C exhibit a clear absorption edge at deep ultraviolet region around 250–275 nm wavelength. High resolution transmission electron microscope (HRTEM) images and X-ray diffraction (XRD) patterns demonstrate that β -Ga₂O₃(-201)//Al₂O₃(0001) epitaxial texture dominated the epitaxial oxide films on sapphire substrate, which opens up the possibilities of high power electric devices.

Keywords: Oxide semiconductor; β -Ga₂O₃ epitaxy; optical transmission spectrum; pulsed laser deposition; crystal growth.

1. Introduction

Wide band gap semiconductors, so-called the third generation of semiconductor materials, are playing important roles in applications of short-wavelength light emission devices, such as, ultraviolet LED and laser diode (LD). Following the success of GaN-based materials, oxide semiconductor films have attracted more and more attentions because of their excellent properties. Gallium oxide (Ga₂O₃) is considered as one of the most promising materials in oxide microelectronics and optoelectronics due to a combination of unique material properties and substrate availability. Ga₂O₃ has five polymorphs.¹ β -Ga₂O₃ is the most stable monoclinic crystal structure, with high dielectrics constant (9.9–10.2)² and high breakdown voltage (8 MV/cm),³ good thermal and chemical stability, as well as a wide band gap of 4.9 eV.⁴ Due to a large amount of oxygen vacancies present in the as-deposited films, un-intentionally doped (UID) gallium oxides usually behave as n-type semiconductors.⁵ To achieve high quality crystalline oxide film through epitaxial growth, two key factors

should be considered: one is the technique of growth, and the other is the choice of the substrates. In recent years, various methods of growth have been used for epitaxial growth of Ga₂O₃ films, for example, metal organic chemical vapor deposition (MOCVD),⁶ RF magnetron sputtering,⁷ chemical vapor deposition (CVD),⁸ atomic layer deposition (ALD),⁹ molecular beam epitaxy (MBE)^{10,11} and pulsed laser deposition (PLD).^{12–14} Among them, PLD technique has many advantages for oxide film deposition, such as, easy to use, high deposition rate, low growth temperature, and no limit to the types of target material. As for substrates, lattice constant matching and the thermal properties between oxide films and substrates should be considered first. Therefore, bulk Ga₂O₃ substrates should be perfect for homo-epitaxial growth of high quality Ga₂O₃ thin films. From the device application point of view, however, the poor thermal conductivity of Ga₂O₃ substrates is obviously a drawback. Sapphire substrate has better thermal conductivity than Ga-oxide, and is also commonly used as low-cost substrate. So, it should be of significance to improve the quality of hetero-epitaxial Ga₂O₃

films on sapphire substrate, hopefully to be comparable to homo-epitaxial Ga_2O_3 films. The relatively small lattice mismatch of 6.6% between $\beta\text{-Ga}_2\text{O}_3$ (-201) and Al_2O_3 (0001),¹⁵ as well as the similar thermal expansion coefficients of $\beta\text{-Ga}_2\text{O}_3$ ($\alpha_c = 3.15 \times 10^{-6} \text{ K}^{-1}$)¹⁶ and Al_2O_3 ($\sim 4.3 \times 10^{-6} \text{ K}^{-1}$), make it possible to achieve high quality crystalline Ga_2O_3 films on good thermal conducting substrate for power device applications. Actually, for hetero-epitaxial growth, preparation of the substrate surface is a critical procedure. In this work, we have paid great attentions on substrate preparation in order to obtain atomically cleaned and ordered surfaces of $\beta\text{-Ga}_2\text{O}_3$ and Al_2O_3 (0001). Gallium oxide films were first deposited on $\beta\text{-Ga}_2\text{O}_3$ (100) substrates, and then on Al_2O_3 (0001) substrates for hetero-epitaxial growth. The deposition parameters were optimized by varying growth temperature and oxygen partial pressure. The effects of substrate pretreatment on the quality and properties of epitaxial oxide were also studied, in order to get high quality crystal Ga_2O_3 thin films for novel applications in deep-ultraviolet photodetectors and high power electric devices.

2. Experimental

The oxide film deposition was conducted by using a high-vacuum PLD system, equipped with a KrF excimer laser (248 nm wavelength, 25 ns pulse duration, 2 Hz pulse repetition rate). A nominally stoichiometric ceramic Ga_2O_3 target of 99.99% purity was placed in parallel to the substrate at a distance of 50 mm. Two different kinds of substrates ($\beta\text{-Ga}_2\text{O}_3$ and Al_2O_3) were used for the epitaxy, and the basic PLD recipe is listed in Table S1 (detailed are shown in supporting information). All the substrates were first cleaned by sonication in acetone, isopropyl alcohol and deionized water for 10 min, respectively, then followed by pure N_2 blowing. After loading the substrates in, the deposition chamber was evacuated to $2.0 \times 10^{-6} \text{ Pa}$ quickly by a turbo molecular pump. The laser beam was focused on the rotated Ga_2O_3 target at an incidence angle of 45° , and pre-sputtered the target for 10 min in order to remove the surface contaminations. All the oxide films were characterized first by using

conventional θ - 2θ scan of X-ray diffraction (XRD), equipped with copper $\text{K}\alpha$ emission line ($\lambda = 0.154056 \text{ nm}$). The samples were tilted for 2° to avoid strong diffraction signals from substrates. The crystallinity of the film was further evaluated by X-ray rocking curve (XRC) of high resolution double-crystal method. High resolution transmission electron microscopy (HRTEM) was employed to reveal the atomic structures of the oxide films and the epitaxial interfaces. X-ray photoelectron spectroscopy (XPS) (PHI 5000 VersaProbe II, ULVAC-PHI Inc.) was used to analyze the chemical states and composition of the films. The surface morphology and roughness were examined by atomic force microscope (AFM), the homo- and hetero-epitaxial AFM results are presented in Figs. S2 and S4 of the supporting information.

3. Results and Discussion

3.1. Gallium oxide deposited on $\beta\text{-Ga}_2\text{O}_3$ (100) substrate

Homo-epitaxial growth generally produces high quality crystal films due to the perfect lattice and thermal matches. $\beta\text{-Ga}_2\text{O}_3$ crystalline substrates are commercially available. The deposition parameters were optimized by varying the growth temperature and the oxygen partial pressure. FWHMs of the homo-epitaxial thin films of the $\beta\text{-Ga}_2\text{O}_3$ (400) peaks deposited at $650\text{--}750^\circ\text{C}$ are $0.155^\circ\text{--}0.193^\circ$, the homo-epitaxial thin films are considerable smooth with small root-mean-square (RMS) roughness between 0.43 nm and 1.43 nm (details are shown in Figs. S1 and S2 of supporting information). The best conditions we found are $650\text{--}700^\circ\text{C}$ and 0.5 Pa for homo-epitaxial growth. The SEM cross-section in Fig. 1(a) of the homo-epitaxial $\beta\text{-Ga}_2\text{O}_3$ film, grown at 650°C and 0.5 Pa of oxygen partial pressure, displays the differentiable interface between the epitaxial film and the substrate, as well the film thickness as about 31.3 nm. The HRTEM image of this homojunction structure, as shown in Fig. 1(b), indicates the superiority of homo-epitaxial growth to get high quality oxide crystalline thin films. In the enlarged HRTEM image, the interplanar distances marked as 0.281 nm and 0.583 nm correspond to d-spacing of monoclinic $\beta\text{-Ga}_2\text{O}_3$ (002) and (200) planes, respectively, which is

Fig. 1. (a) SEM cross-section image of homo-epitaxial $\beta\text{-Ga}_2\text{O}_3$ thin film (b) the HRTEM image demonstrate single crystalline $\beta\text{-Ga}_2\text{O}_3$ formed at 650°C and 0.5 Pa of oxygen partial pressure.

in good agreement with the results previously reported by Hosein *et al.*¹⁷

3.2. Gallium oxide deposited on sapphire substrate

Sapphire crystal is a kind of substrate commonly used for epitaxial growth of semiconductor thin films, and has better thermal conductivity than β -Ga₂O₃ substrate. Epitaxial growths of β -Ga₂O₃ films on sapphire substrates were reported already, although the crystal quality was not good enough.^{18,19} One of the key factors that affect epitaxial film quality is the surface condition of substrate. Sapphire substrates were usually pre-treated either by high temperature annealing,²⁰ or wet chemical etching.^{21,22} By combining and optimizing the two kinds of pre-treatment methods, we observed clearly terraced surface of Al₂O₃ substrate. AFM image of the sapphire substrate for atomic terraced surface are shown in Fig. S3 of supporting information. However, there is no terrace-like morphology observed on the sapphire substrate if only treated generally by chemical clean. By taking the optimized parameters, we deposited Ga-oxide films on Al₂O₃ (0001) surfaces with and without atomic terraces for comparison. In Fig. 2(a), both kinds of films show clearly β -Ga₂O₃ diffraction peaks ($\bar{2}01$, $\bar{4}02$, and $\bar{6}03$), indicating crystalline gallium oxide films formed. However, the diffraction peaks of β -Ga₂O₃ on the terraced Al₂O₃ substrate pretreated with the full-process (chemical clean plus annealing) are much sharper than that on the Al₂O₃ substrate pretreated only by organic solvents. Figure 2(b) shows the rocking curves of ($\bar{2}01$) diffraction peak of the two films, and the FWHM is 1.1° and 1.8°, respectively, for the β -Ga₂O₃ epitaxial films grown on the full-process treated and organic solvents only cleaned sapphire substrates. The FWHM of hetero-epitaxial film is larger than that of homo-epitaxial film and the FWHM is smaller by atomic terraced surface of sapphire substrate. The crystal quality of β -Ga₂O₃ film could be remarkably improved by using the atomic

terrace surface of sapphire substrate, which can be explained by a theory of low free surface energy.²³

To further optimize the growth parameters, we also studied the effects of temperature and oxygen pressure on the film crystallization. Figure 3(a) shows the XRD patterns of the gallium oxide films deposited at various temperatures. All the diffraction peaks represent the ($\bar{2}01$) plane family of β -Ga₂O₃, matching well with those in the PDF card (No: 43-1012) and consisting with previous reports²² too. However, the quality of film grown at 600°C is obviously inferior, comparing with that grown at 700°C and 750°C, as indicated by the extra (400) peak and larger FWHM of ($\bar{2}01$) peak. Besides temperature, the oxygen partial pressure is another key factor responsible to the film quality. As shown in Fig. 3(b), over-pressure makes the diffraction peak broad and even produces other peaks rather than the ($\bar{2}01$) series. As summarized in Table 1, the grain size of all of those films could be induced from the FWHM values of ($\bar{2}01$) diffraction peaks, according to Scherrer equation

$$D = \frac{0.89\lambda}{\beta \cdot \cos \theta}, \quad (1)$$

where D , λ , β and θ are average crystalline grain size, X-ray wavelength, FWHM of diffraction peak and Bragg diffraction angle, respectively.

Corresponding to the grain size variation among these films, the surface roughness was also evaluated by using AFM (detailed results are presented in Fig. S4 of the supporting information). The film surfaces are smoother at higher growth temperature and lower oxygen pressure. Those results suggest that high quality films could be grown on sapphire substrate at 650–700°C and 0.5 Pa oxygen pressure, the similar conditions optimized for homo-epitaxial growth. At lower temperature, thermal energy is not enough to supply the ad-atomic migration, leading to poor crystallization. With temperature increasing, high thermal energy enhances the surface mobility of ad-atoms, making the crystallization

Fig. 2. XRD spectra of β -Ga₂O₃ epitaxial films (700°C–0.5 Pa) grown on the organic cleaning only and full-process treated sapphire substrates: (a) 2θ scan and (b) ω scan (red line represents the substrate with atomic step processing, black line represents the substrate with organic cleaning).

Fig. 3. XRD patterns of the gallium oxide films deposited (a) at different substrate temperatures; (b) at different oxygen pressures.

Table 1. Characteristics of β -Ga₂O₃ thin film deposited at various conditions.

Substrate temperature (°C)	Grain size (nm)	FWHM (°)	XPS O/Ga ratio	Roughness (nm)
600 (0.5 Pa)	18.9	0.439	1.32	2.25
700 (0.5 Pa)	27.6	0.309	1.34	1.38
750 (0.5 Pa)	23.1	0.364	1.34	4.75
750 (2 Pa)	20.1	0.414	1.32	2.45
750 (10 Pa)	13.1	0.648	1.30	22.9

improved. However, if the temperature further increases, the atomic migration could be too fast to form regular bonds of single crystal. In addition, high temperature leads more thermal defects, declining the crystal quality.²⁴ On other hand, with the oxygen partial pressure increases, the crystal quality of β -Ga₂O₃ degrades probably due to the surface ad-atomic mobility becoming low, and/or the collision of oxygen atoms with the plasma (ions/atoms) getting intense.

To check the in-plane atomic structure, Fig. 4(a) shows the Φ scan at a slant angle of 23.51°, with six peaks that appear approximately every 60°, indicating six fold in-plane rotational symmetry. Since the monoclinic β -Ga₂O₃ {401} planes have only two-fold in-plane rotational symmetry, we

could conclude that the film contains three-folded domains, originated from the three-fold rotational c-sapphire substrate. Two-folded planes with three-folded domains result in six almost equally separated peaks in the Φ scan measurements, similar as the conclusions reported by Zhang *et al.*²¹ and Oshima *et al.*²⁵ XPS analysis was conducted to characterize the films' stoichiometry chemical states. All the spectra were calibrated to compensate the surface charge effect with C1s peak of 284.8 eV as the reference. By normalizing and overlapping the major core-level peaks of Ga3d and O1s, respectively, there is not much difference observed between films grown at different temperatures or with different oxygen partial pressures. These peaks were further deconvoluted by

Fig. 4. (a) XRD in-plane Φ scan of β -Ga₂O₃ (-401) diffraction on the film grown at 700 °C; High resolution XPS core-level spectra of Ga3d (b) and O1s (c) in Ga₂O₃ films deposited at temperature of 700 °C and oxygen partial pressure of 0.5 Pa. A set of Gaussian (70%)/Lorentzian (30%) line shapes used for curve fitting.

Fig. 5. (a) Cross-section SEM image, and (b) HRTEM images of β -Ga₂O₃ thin film deposited on Al₂O₃ (0001) substrate at 700°C and 0.5 Pa of oxygen.

using CasaXPS program, with Gaussian–Lorentzian peak shape and Shirley type background subtraction. Taking the thin film deposited at 700°C and 0.5 Pa oxygen as an example, the Ga3d peak in Fig. 4(b) is composed of three components, Ga–O bond at 20.1 eV^{26,27} Ga–Ga bond at 18.1 eV, and O2s peak at 22.8 eV; the O1s peak in Fig. 4(c) is

Fig. 6. Transmittance spectra of hetero-epitaxial Ga₂O₃ films grown at various temperatures (650–750°C).

composed of two components, O–Ga bond at 530.8 eV and O–H bond at 532.6 eV.²⁸ The binding energies of Ga3d(O) and O1s(Ga) are in agreement with the reported binding energy values of β -Ga₂O₃²⁹ and the intensity ratio of [O1s(Ga)]/[Ga3d(O)] is about 1.34 ± 0.02 . This value closes enough to the ratio for stoichiometric Ga₂O₃, considering the quantitative analysis error of XPS.

Similarly, as that for the homo-epitaxial growth, SEM and HR-TEM were conducted for the hetero-epitaxial β -Ga₂O₃ film grown on Al₂O₃ (0001) at 700°C and 0.5 Pa of oxygen pressure. As displayed in Fig. 5(a), the SEM cross section image shows an oxide film of ~110 nm and a clear interface between β -Ga₂O₃ and Al₂O₃ substrate. The HR-TEM image in Fig. 5(b) shows that the oxide film is not a perfect single crystal, but a β -Ga₂O₃(-201)//Al₂O₃(0001) epitaxial texture dominated crystal film, which is in agreement with the Φ scan results and also consistent with the results reported by Huang *et al.* previously.³⁰

During the growth of the β -Ga₂O₃ films on Al₂O₃ substrates at various substrate temperatures of 600°C, 700°C, and 750°C. Here the growth oxygen pressure was set to 0.5 Pa. From Fig. 6, the clear Optical transmittance deposited

Fig. 7. (a) $(ah\nu)^2-h\nu$ plot of hetero-epitaxial β -Ga₂O₃ films deposited at various temperatures of 650–750°C. (b) corresponding band gap as a function of substrate temperatures.

at 600°C, 700°C and 750°C, Transmittance spectra of the films prepared at various substrate temperatures are plotted in Fig. 6. The transmittances of all samples in infrared region are above 80%, and exhibit clear fringes in the visible and UV regions. Therefore, in this work the β -Ga₂O₃ films were grown at the optimum substrate temperature of 700°C, to ensure good crystal quality.

The optical band gap can be obtained by extrapolating the linear region near the onset in a plot of α^2 versus $h\nu$, as shown in Fig. 7(a). The E_g values are 5.07, 5.17, 5.20 eV as the β -Ga₂O₃ thin films grown at 600°C, 700°C and 750°C, respectively, as shown in Fig. 7(b). The band gap value about 4.9 eV at 600–750°C agrees with that of bulk Ga₂O₃. It shows that the absorption edges are shifted towards short wavelength region (blue shift), i.e., increase in the band gap energy with increasing substrate temperature.

4. Conclusions

In summary, high quality stoichiometric β -Ga₂O₃ thin films were deposited on β -Ga₂O₃ (100) and Al₂O₃ (0001) substrates, respectively, by using PLD method at a temperature between 650–700°C and oxygen partial pressure of 0.5 Pa. The homo-epitaxial β -Ga₂O₃ film on β -Ga₂O₃ (100) substrate is single crystal as confirmed by XRD and HRTEM. For hetero-epitaxy, β -Ga₂O₃/Al₂O₃ (0001) texture dominated crystal film was formed with the similar growth conditions as that for homo-epitaxy, and the crystalline quality was obviously improved for film grown on atomic terraced sapphire substrate surface. It is believed that high quality gallium oxide films could be achieved through either homo- or hetero-epitaxial growth, and will be widely adopted to develop novel deep ultraviolet optoelectronic and high power electric devices.

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