Growth and etching characteristics of (001) β-Ga_2O_3 by plasma-assisted molecular beam epitaxy

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We investigated the homoepitaxial growth and etching characteristics of (001) β-Ga_2O_3 by plasma-assisted molecular beam epitaxy. The growth rate of β-Ga_2O_3 increased with increasing Ga-flux, reaching a clear plateau of 56 nm/h, and then decreased at higher Ga-flux. The growth rate decreased from 56 nm/h to 42 nm/h when the substrate temperature was increased from 750 to 800 °C. The growth rate was negative (net etching) when only Ga-flux was supplied. The etching rate proportionally increased with increasing the Ga-flux, reaching 84 nm/h. The etching was enhanced at higher temperatures. It was found that Ga-etching of (001) β-Ga_2O_3 substrates prior to the homoepitaxial growth markedly improved the surface roughness of the film.

1. Introduction

β-Ga_2O_3 is attracting remarkable attention for its great potential to realize high-performance power devices due to its large band gap ($E_g \sim 4.7$ eV) [1] and availability of melt-grown high-quality single crystal substrates [2-5]. (010) β-Ga_2O_3 substrates are used in most cases to fabricate β-Ga_2O_3 power devices such as Schottky barrier diodes (SBD) [6], and field effect transistors (FET) [7].

Currently, the edge-defined film-fed growth (EFG) method is used to produce commercial β-Ga_2O_3 single crystal substrates [3,4]. This growth method gives board-shaped crystal with a thickness of up to a few centimeters. In melt growth techniques of β-Ga_2O_3, the crystal pulling (growth direction) needs to be toward the unique b-axis (*i.e.*, [010] direction) so that the cleavage planes (100) and (001) are parallel to the growth direction to prevent twinning and formation of small angle grain boundaries. The area of EFG-grown (010) β-Ga_2O_3 wafers, so far, has been limited to around 10×15 mm^2. Therefore, it is difficult to produce large-area (010) β-Ga_2O_3 wafers with a diameter of 6 inches or more, which will be required for the mass production of β-Ga_2O_3 power devices. The Czochralski (Cz) method is also under investigation [5]. The challenges for Czochralski growth of β-Ga_2O_3 include difficulties in damage of the iridium crucibles, which is strongly enhanced with increasing the melt volume [8].

In contrast, there is no fundamental limitation to produce large-area β-Ga_2O_3 wafers with a principal crystal plane in the [010] zone (e.g., planes (*h*0*l*)) by the EFG method. In practice, EFG-grown 6-inch $(\bar{2}01)$ bulk crystal has already been demonstrated by the Tamura Corporation. Unfortunately, $(\bar{2}01)$ homoepitaxial layers suffered from a high density of stacking faults [9]. The (100) plane is also in the [010] zone. However, the MBE growth rate on the (100) plane is extremely small because of the preferential formation of volatile suboxide Ga_2O, and (100) is not suitable for industrial use [6,10]. We therefore need to explore other crystal planes to enable high-quality epilayers which can be grown at reasonable growth rates.

In this work, we focus on growth on (001) oriented β-Ga_2O_3 substrates, which are also in the [010] zone and thus are scalable. In practice, Tamura Corporation has successfully grown large-size (001) β-Ga_2O_3 board-like bulk crystals by EFG method and high-quality 2-inch (001) β-Ga_2O_3 wafers are commercially available. In addition, Konishi *et al.* demonstrated (001) β-Ga_2O_3 SBDs with breakdown voltage of over 1 kV using homoepitaxial film grown by halide vapor phase epitaxy [12]. Hence, (001) is promising for power device applications. To fabricate FETs or high electron mobility transistors (HEMTs) using (001) β-Ga_2O_3, we need to develop thin film growth technologies for (001) β-Ga_2O_3. Molecular beam epitaxy (MBE), which enables precise thickness control and abrupt interfaces, is advantageous for such purpose. The present work investigates positive and negative growth (*i.e.* etching) characteristics of (001) β-Ga_2O_3 by MBE.

2. Experimental

β-Ga_2O_3 was grown on EFG-grown (001) β-Ga_2O_3 single crystal substrates by plasma-assisted MBE (PA-MBE) at substrate temperatures T_s = 700 ~ 800 °C. Each β-Ga_2O_3 substrate was indium-bonded on a Si backing wafer. T_s was measured by a thermocouple located near a heater behind the backing wafer. Metallic aluminum (melting temperature

660°C) on a β-Ga_2O_3 substrate melted at T_s = 645°C. The Ga flux was supplied using conventional K-cells. Beam equivalent pressure (BEP) of the Ga-flux P^0_{Ga} was 1.7×10^{-8} ~ 9.5×10^{-8} Torr. Plasma-activated oxygen, presumably atomic oxygen, was supplied from a Veeco Uni-bulb oxygen RF-plasma source. The oxygen foreline pressure and RF plasma power were 60 Torr and 200 W, respectively. The Ga-flux, oxygen plasma supply, and T_s were kept constant throughout the growth. The film thickness was calculated from thickness fringe spacing in high resolution x-ray diffraction (HRXRD) symmetrical ω-2θ scans measured in a triple-axis configuration using Cu Kα_1 radiation. A very thin layer of β-$(Al_xGa_{1-x})_2O_3$ was grown for 1.5 min with Al-flux ratios (the ratio of Al flux to the total group III flux) of 0.021 ~ 0.137 in prior to the growth of β-Ga_2O_3 in order to obtain clear thickness fringes in ω-2θ scans. In the case of (010) β-$(Al_xGa_{1-x})_2O_3$ layers, the Al content x tends to be higher than the Al-flux ratio [13]. In this work, the Al content of the interlayers was not measured, but the tendency should be similar. Typical ω-2θ scan profile is shown in Fig. 1. The surface morphology was observed by atomic force microscopy (AFM).

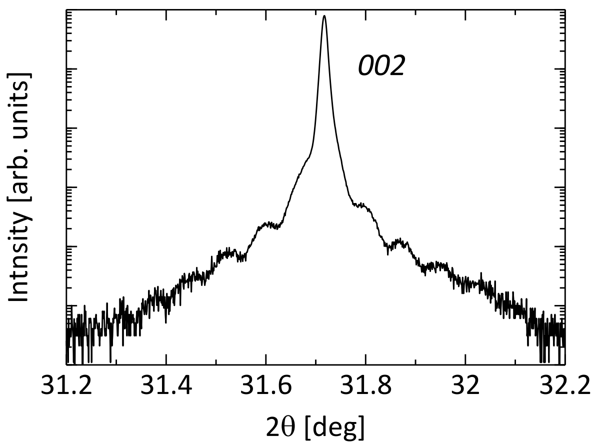

Figure 1. XRD ω-2θ scan profile of a (001) β-Ga_2O_3 homoepitaxial wafer.

3. Results and discussion

Figure 2 shows the dependence of the growth rate of (001) β-Ga_2O_3 on P^0_{Ga} at T_s = 750 °C. Our results on (100) [10] and (010) [11] planes are also shown for comparison. The growth rate on (001) first increased with increasing P^0_{Ga}, reaching clear plateau, and then decreased at higher P^0_{Ga}. It has been reported that the dependence of growth rate on P^0_{Ga} for $(\bar{2}01)$ β-Ga_2O_3 homoepitaxial growth shows similar behavior, and growth rate decrease in Ga-rich condition can be attributed to the formation of volatile suboxide Ga_2O [14]. Thermodynamic analysis of PA-MBE of Ga_2O_3 tells us that the formation of Ga_2O is favored in the Ga-rich regime, and the growth rate should decrease with increasing P^0_{Ga} [15]. However, the thermodynamic analysis does not predict the plateau. The existence of the plateau indicates that Ga_2O starts to form even in O-rich conditions. Vogt *et al.* pointed out that the $(\bar{2}01)$ β-Ga_2O_3 surface could act as a catalyst for Ga_2O formation [14]. It is likely that a similar phenomenon is taking place also on (001) β-Ga_2O_3. Such catalytic effect could be different depending on the crystal plane and result in different growth rates. The growth rate at the plateau was approximately 56 nm/h, which is about 1/4 of that on (010), and about twice of that on (100) under similar growth conditions. Using ozone MBE, Sasaki *et al.* investigated the growth rate of β-Ga_2O_3 for various crystal planes, and the trend shown here agrees with their results [6].

When oxygen plasma was not supplied, the growth rate was negative. The etching rate was estimated by comparing the homoepitaxial film thickness before and after the 30 min etching. The film thickness was measured by the method described in the experimental part. It was confirmed that no measurable etching took place even at T_s = 850°C when neither Ga-flux nor oxygen plasma was supplied. The etching rate proportionally increased with increasing P^0_{Ga}, reaching 84 nm/h. This phenomenon can be utilized as a clean etching technique. This "Ga-etching technique" uses no contaminant, and can be carried out in MBE chambers. Therefore, it is possible to reduce surface contamination of β-Ga_2O_3 substrates just before the MBE growth. CMP-related damage could also be removed. The Ga-etching can be applied not only to (001) but also to other crystal planes, such as (010). We have applied this technique to decrease the Si accumulation on (010) β-Ga_2O_3 surface, and successfully demonstrated a modulation-doped FET [16].

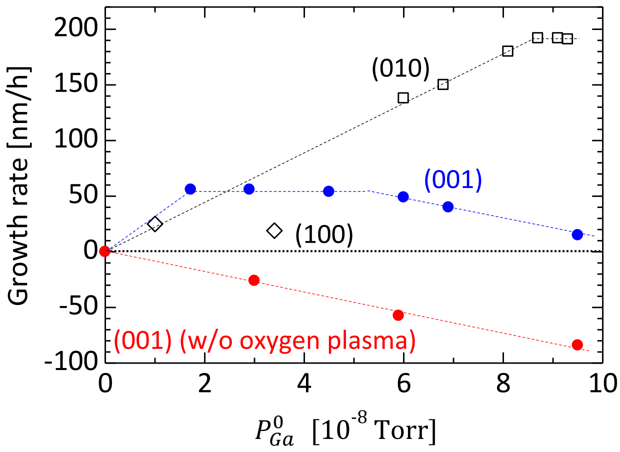

Figure 2. Growth rate of β-Ga_2O_3 as functions of P^0_{Ga}. Foreline oxygen pressures were 60 Torr for (010) and (001) samples, and 50 Torr for (100) samples. RF plasma power was 200W. Broken lines are guides for eyes.

Figure 3 shows the dependence of the growth rate of (001) β-Ga_2O_3 on substrate temperature T_s. The growth rate decreased with increasing T_s. Figure 4 shows the dependence of the etching rate of (001) β-Ga_2O_3 on substrate temperature T_s. The etching rate increased with increasing T_s. The thermodynamic calculation does not predict significant increase of Ga_2O formation with increasing T_s in the investigated temperature range [15]. It would be possible that the catalytic effect of Ga_2O_3 surface is enhanced at higher temperatures and results in reduced growth rate.

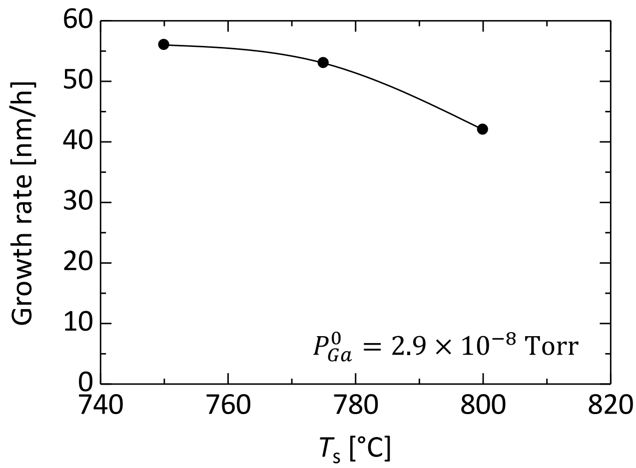

Figure 3. Growth rate of (001) β-Ga_2O_3 as a function of substrate temperature T_s.

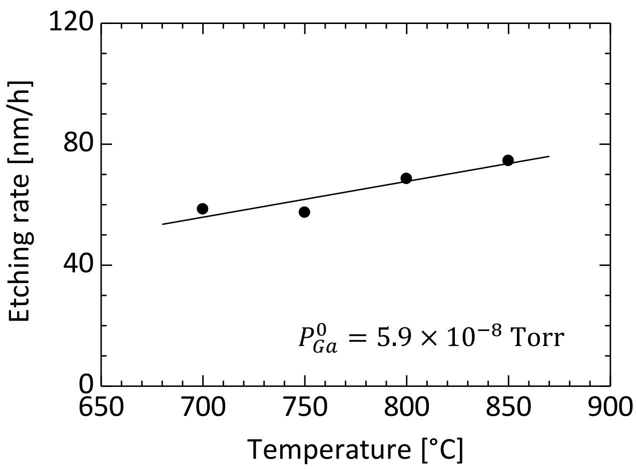

Figure 4. Etching rate of (001) β-Ga_2O_3 as a function of substrate temperature T_s.

Figures 5 (a), (b) and (c), (d) show AFM images of a virgin (001) β-Ga_2O_3 substrate and Ga-etched surface of the same substrate respectively. The rms roughness of the virgin substrate was 0.2 nm, and the miscut was 0.03° in an azimuthal direction 63° clockwise from [010] to [100]. The etching was carried out with P_{Ga}^{0} = 5.9×10^{-8} Torr at T_s = 750 °C for 30 min. Under these conditions, the etched depth should be 29 nm. The rms roughness did not show significant increase by the Ga-etching although the step-terrace structure became less clear.

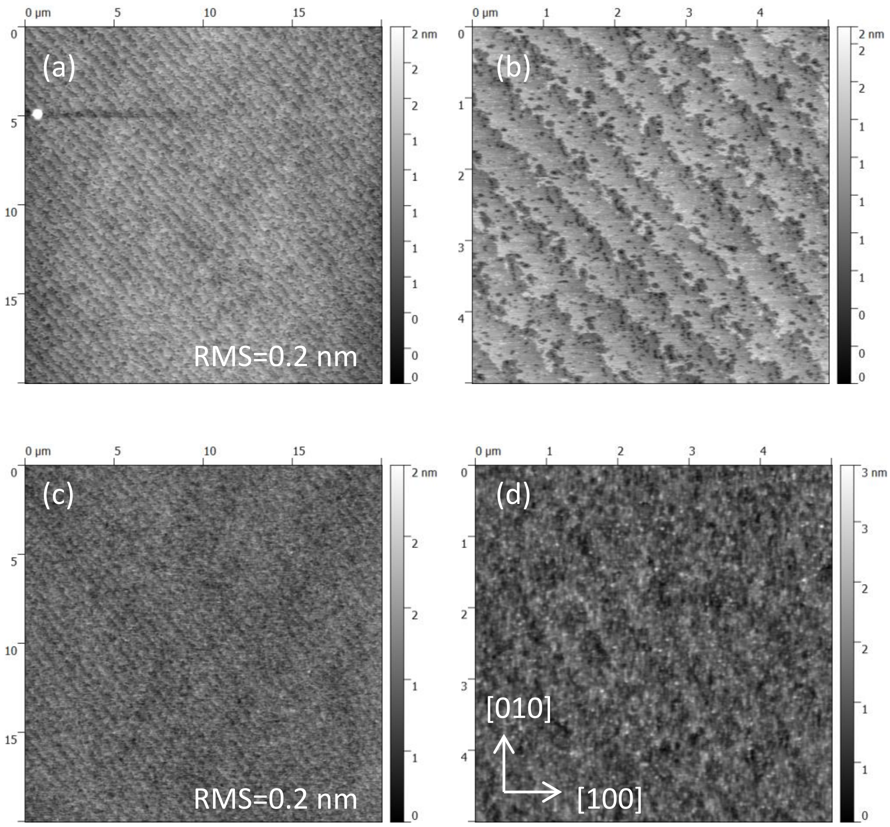

Figure 5. AFM images of a (001) β-Ga_2O_3 substrate. (a),(b): virgin substrates, (c),(d): After Ga-etching (-29 nm)

Figures 6 (a) and (b) show AFM images of homoepitaxial (001) β-Ga_2O_3 layers grown on a virgin (001) β-Ga_2O_3 substrate and Ga-etched one, respectively. The Ga-etched substrate was the same one shown in Figs. 5 (c) and (d). The films were grown with P_{Ga}^{0} = 2.9×10^{-8} Torr at T_s = 750 °C (56 nm/h) for 2 hrs. The film grown on a virgin substrate tends to be bumpy. On the other hand, the Ga-etched substrate gave very smooth film surface with rms roughness of ~0.2 nm. We speculate that the Ga-etching could remove surface contamination and/or polish-related damage, and resulted in the smooth surface. Stripe-like morphological features along [010] were observed on the surface. The direction of the stripes is different from the miscut direction. This is probably because the formation of such morphology should be attributed to the (100) faceting, which is also observed on HVPE-grown (001) homoepitaxial films [17].

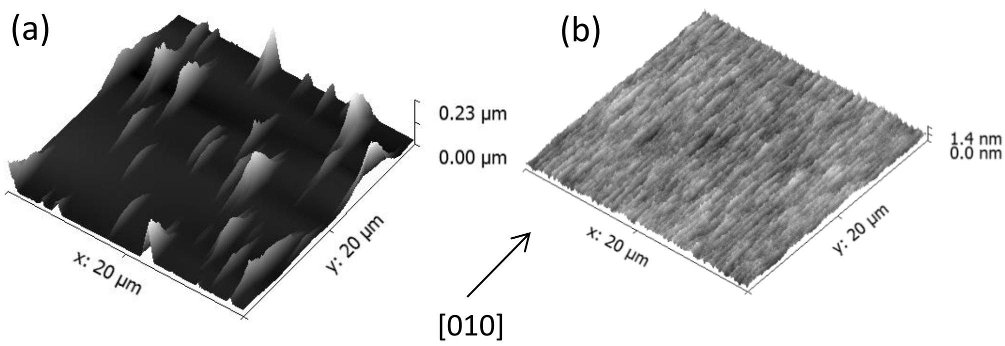

Fig. 6 AFM images of (001) β-Ga_2O_3 films grown on (a) virgin substrate, (b) Ga-etched substrate

4. Summary

In summary, growth and etching characteristics of (001) β-Ga_2O_3 was investigated by PA-MBE. The Ga-flux dependence of the growth rate exhibited clear plateau, probably due to the preferential formation of volatile suboxide Ga_2O. The growth rate was negative when oxygen plasma was not supplied, and the etching rate increased proportionally to the Ga-flux. The rms roughness did not show significant increase after the Ga-etching. The rms roughness of homoepitaxial layer was markedly improved by the Ga-etching prior to the growth.

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Figure captions

Fig. 1 XRD ω-2θ scan profile of a (001) β-Ga_2O_3 homoepitaxial wafer.

Fig. 2 Growth rate of β-Ga_2O_3 as functions of P_{Ga}^0. Foreline oxygen pressures were 60 Torr for (010) and (001) samples, and 50 Torr for (100) samples. RF plasma power was 200W. Broken lines are guides for eyes.

Fig. 3 Growth rate of (001) β-Ga_2O_3 as a function of substrate temperature T_s.

Fig. 4 Etching rate of (001) β-Ga_2O_3 as a function of substrate temperature T_s.

Fig. 5 AFM images of (001) β-Ga_2O_3 substrates. (a),(b): virgin substrates, (c),(d): After

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