

Visualization of threading dislocations in an α -Ga₂O₃ epilayer by HCl gas etching

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Abstract

Threading dislocations in a heteroepitaxial α -Ga₂O₃ film was visualized as etch pits on the surface.

We found that etch pits were formed on a *c*-plane α -Ga₂O₃ epilayer by HCl gas etching. The epilayer was prepared by using epitaxial lateral overgrowth technique with a stripe mask pattern. The etch pit density was very high in the window region, and much lower in the laterally grown area on the mask.

A line of etch pits was observed at a coalesced boundary. Thus, the etch pit density had a clear correlation with the dislocation density. The correspondence between the etch pits and dislocations was confirmed by cross-sectional bright- and dark-field transmission electron microscopy (TEM).

This gas-etching technique can clarify the distribution of dislocations in a wide area, which cannot be explored effectively by TEM.

Keywords

A3. Hydride vapor phase epitaxy; A3. Selective epitaxy; B1. Gallium compounds; B1. Oxides; B2.

Semiconducting gallium compounds

1. Introduction

Corundum-structured α -Ga₂O₃ is an ultra-wide bandgap semiconductor with an energy gap of $E_g = 5.3$ eV [1], and is promising for power devices and UV detectors. Indeed, Schottky barrier diodes (SBDs) with very low on-resistance and high-performance UV detectors have already been demonstrated [2,3]. Engineering samples of α -Ga₂O₃-based SBDs have been shipped, and evaluation boards with a power function correction (PFC) circuit using the SBDs are commercially available [4]. An α -(Al_xGa_{1-x})₂O₃ solid solution can be grown without any limitation of the aluminum composition x [5], while x is limited to ~40% in the case of β -(Al_xGa_{1-x})₂O₃ [6]. Therefore, the α -phase is advantageous to make heterostructures, which should be useful in improving the device performance. It is also possible to produce a hetero pn-junction using p-type corundum-structured compounds, such as α -(Ir_yGa_{1-y})₂O₃ [7,8], and α -Ga₂O₃-based normally-off metal-oxide-semiconductor field effect transistors with a p-type well layer have been demonstrated [9].

α -Ga₂O₃ is metastable under ambient pressure [10], and therefore melt-grown homoepitaxial substrates are not available in contrast to the case with β -Ga₂O₃ [11-14]. Accordingly, an α -Ga₂O₃ film needs to be grown heteroepitaxially. Mist chemical vapor deposition, halide vapor phase epitaxy (HVPE), and molecular beam epitaxy have been mainly reported as the growth methods [1, 15-18]. Sapphire is commonly used as a substrate to grow an α -Ga₂O₃ film because the crystal structure is the

same as that of α -Ga₂O₃, and large-area wafers are commercially available at a reasonable price.

However, the threading dislocation density in a heteroepitaxial α -Ga₂O₃ film is as high as 1×10^{10} cm⁻² because of the large lattice mismatch ($\Delta a/a \sim 4.5\%$, $\Delta c/c \sim 3.3\%$) if no measure is taken [19].

The epitaxial lateral over-growth (ELO) technique is effective to reduce the dislocation density [19-23]; however, this technique needs to be further improved to achieve a lower dislocation density in a wider area.

To decrease the dislocation density in α -Ga₂O₃, it is essential to clarify the dislocation distribution in the target epilayer. Transmission electron microscopy (TEM) is one of the most powerful methods for this purpose. TEM can visualize the distribution and identify the dislocation character. However, the observable area is usually limited to below $\sim 10 \times 10 \mu\text{m}^2$. Upon conducting ELO, the mask fill factor should be small (*i.e.*, a wide mask with narrow windows) to effectively reduce the dislocation density. Accordingly, the mask width can be over several tens of micrometers [21]. In such a case, TEM is not appropriate to clarify the whole picture of the dislocation distribution. X-ray diffraction (XRD) is also a useful method. It is possible to estimate the density of dislocations having edge/screw components from the FWHMs of the X-ray rocking curves measured in the out-of-plane/in-plane diffraction geometry, respectively [24, 25]. The measurement area depends on the optical system settings, and it is typically much larger (mm²–cm²) than that of TEM. However, the data obtained by XRD are a

superposition of the information distributed in the detected area. Therefore, it is difficult to clarify the dislocation distribution on the microscopic scale. Inhomogeneity along the film thickness can also affect the data because of the penetration of X-rays.

In the case of conventional semiconductor materials such as GaN, the etch pit method has been well established to clarify the dislocation distribution in a large area. The etching can be wet using, for example, KOH or H₃PO₄, or dry using HCl gas [26, 27]. It is also possible to identify the dislocation character on the basis of the etch pit shape. Note that the diameter of the etch pits should be μm -size or larger for the convenience of wide-area observation by scanning electron microscopy (SEM) or optical microscopy. In this case, the etch pit density should be less than $\sim 10^8 \text{ cm}^{-2}$ to avoid the overlapping of the pits and to accurately estimate the density.

Our purpose in the present work is to establish an etch pit method for $\alpha\text{-Ga}_2\text{O}_3$. The formation of etch pits on $\alpha\text{-Ga}_2\text{O}_3$ has already been reported by Kawara et al [28]. They made etch pits on an ELO-grown $\alpha\text{-Ga}_2\text{O}_3$ sample using a KOH aqueous solution and visualized the anisotropic etch pit distribution over an area of $20 \times 20 \mu\text{m}^2$. However, a correspondence between the etch pits and dislocations has not yet been confirmed by TEM. In addition, attention should be paid to avoid surface contamination by the etchant if the sample is further used for surface-chemical-sensitive

characterizations such as X-ray photoelectron spectroscopy and photoluminescence. From this point of view, the gas-etching technique should be better. However, no such report has been made for α -Ga₂O₃. Note that cathode-luminescence or microscopic photoluminescence, which are very powerful tools to visualize the dislocation distribution in typical direct-transition-type semiconductors, such as GaN [29, 30], are not appropriate for α -Ga₂O₃ because this material does not exhibit band-edge emission.

As a result of the present work, we have successfully formed etch pits on ELO-grown α -Ga₂O₃ samples by HCl gas etching. The correspondence between the etch pits and dislocations has been confirmed by cross-sectional TEM. Thus, we have established a useful technique to visualize the dislocation distribution in a wide area.

2. Experimental

First, we prepared a *c*-plane α -Ga₂O₃ / sapphire substrate with TiO_x stripe masks (approximately 50 nm thick) on the top. The mask was along [1 $\bar{1}$ 00], and the mask width was 5 μ m. The mask window was 1 or 5 μ m wide. Then, α -Ga₂O₃ was regrown on the substrate. The epitaxial growth was performed in a lab-made HVPE reactor using GaCl_x and O₂ as the precursors. Details of the sample preparation have been described elsewhere [15, 21]. The etching experiment was performed in a HCl / N₂ mixture

gas stream using the same HVPE reactor as described above. The etching process was conducted independently of a growth run. HCl gas was supplied with a partial pressure of 37.5 Pa at 520 °C for 1 min under atmospheric pressure. Heating up / cooling down steps were carried out in a pure N₂ gas stream. After the etching, the surface morphology was observed by SEM. Correlation between the etch pits and dislocations was investigated by cross-sectional TEM.

3. Results and discussion

3.1 Distribution of dislocations and etch pits

Figure 1 (a)–(c) shows the growth evolution on the stripe mask. The regrowth of α -Ga₂O₃ started selectively from the mask windows to form α -Ga₂O₃ stripes. The α -Ga₂O₃ stripe consisted of (0001) top facet and (11 $\bar{2}$ 0) side facets. Deposition of polycrystalline κ -Ga₂O₃ was observed on the mask between the α -Ga₂O₃ stripes [21]. Then, the stripes grew vertically and laterally to coalesce with each other and form a compact film.

Figure 2 (a)–(c) shows the cross-sectional TEM images of an α -Ga₂O₃ stripe. Fig. 2(a) is a bright-field image. A high density of dislocation was found in the seed layer. A plan-view TEM image (not shown) revealed that the dislocation density was $\sim 1 \times 10^{10} \text{ cm}^{-2}$ [19]. The dislocation density above the mask window was also high because the dislocations in the seed layer directly propagated into the regrown

α -Ga₂O₃. In contrast, the dislocation density was much lower in the laterally grown area on the mask. These dislocations were still visible in the dark-field image taken with a diffraction vector $g = \bar{1}\bar{1}20$ (Fig. 2(b)). However, virtually no dislocation was visible in the dark-field image taken with a diffraction vector $g = 0006$ (Fig. 2(c)). These results indicated that almost all the dislocations in the seed layer and above the window were edge dislocations with Burgers vectors perpendicular to the c -axis. Note that although a part of the dislocations in the window region could bent to propagate into the laterally grown area on the mask, the Burgers vector would not change.

Figure 3(a) and (b) show bird's-eye view SEM images of a coalesced sample grown on the mask with 5- μ m-wide windows before and after the etching, respectively. Before the etching, the surface was relatively rough on the window regions, and much smoother on the laterally grown area on the mask (Fig. 3(a)). After the etching, etch pits were formed. The etch pit density (EPD) was very high on the window regions and the etch pits overlapped with each other (Fig. 3(b)). However, the EPD was much lower on the mask, and isolated etch pits were observed. A line of etch pits was observed at the coalesced boundary. Figure 3(c) and (d) show bird's-eye view SEM images of a coalesced sample grown on the mask with 1- μ m-wide windows before and after the etching, respectively. The tendency of the etch pit distribution was similar, but the high-EPD area was much narrower. The width of the high-EPD area agreed with that of the mask window. These results indicated that the etch pits

corresponded to threading dislocations.

3.2 Origin of the etch pits

Figure 4 shows a magnified SEM image of the etch pits. Three different shapes of the etch pits were observed (Types I, II, and III). Type I, the majority (approximately 95%), had an inverted pyramidal shape with three clear ridges along $\langle 1\bar{1}00 \rangle$. Type II (approximately 3.5%) was smaller than Type I, and had clear contour and a flat bottom. Type III (approximately 1.5%) had unclear contour and a flat bottom with a similar diameter as Type I.

Figure 5(a)–(c) shows cross-sectional TEM images including three Type-I etch pits. The arrows show the positions of the etch pits. In the bright-field image (Fig. 5(a)), it was found that each etch pit was accompanied by a dislocation. All three dislocations were still visible in the dark-field image taken with a diffraction vector $g = \bar{1}\bar{1}20$ (Fig. 5(b)). However, they were invisible in the dark-field image taken with a diffraction vector $g = 0006$ (Fig. 5(c)). Thus, it was found that a Type-I etch pit originated from an edge dislocation.

Figure 6(a)–(c) shows cross-sectional TEM images including a Type-I etch pit and two Type-II etch pits. The arrows show the positions of the etch pits. In the bright-field image (Fig. 6(a)), it was found

that each Type-II etch pit was accompanied by a dislocation as was the case for a Type-I etch pit. All three dislocations were still visible in the dark-field image taken with a diffraction vector $g = \bar{1}\bar{1}20$ (Fig. 6(b)). However, they were invisible in the dark-field image taken with a diffraction vector $g = 0006$ (Fig. 6(c)). Thus, it was found that a Type-II etch pit also originated from an edge dislocation.

Further investigation is required to clarify what causes the shape difference between Types I and II.

Figure 7(a)–(c) shows cross-sectional TEM images including a Type-III etch pit. The arrow shows the position of the etch pit. No dislocation was found under the etch pit in both the bright- and dark-field images. Thus, it was found that a Type-III etch pit did not originate from a dislocation.

Note that no screw- or mixed-dislocation-originated etch pits were found in the present investigation.

This is reasonable because most of the dislocations in the regrown $\alpha\text{-Ga}_2\text{O}_3$, except those at the coalesced boundaries, should be originated from the dislocations in the seed layer, in which virtually no screw components were found by TEM as shown in Fig. 2. Regarding the dislocations at the coalesced boundaries, the vast majority of them should also be edge type because the misorientation between the $\alpha\text{-Ga}_2\text{O}_3$ stripes should possess only a small tilting component considering the dislocation character in the seed layer. Note that the increase of wing tilting during the lateral growth is not observed for ELO-grown $\alpha\text{-Ga}_2\text{O}_3$ in contrast to the case of GaN-ELO [19]. Further research is necessary to clarify the etch pit shapes of a screw or mixed dislocations.

4. Summary

Etch pits were formed on a stripe-ELO-grown (0001) α -Ga₂O₃ film by HCl gas etching, and the cause was investigated. The EPD was very high on the window area, and the width of the high-EPD area agreed with the window width. The EPD was much lower on the laterally grown area on the mask. A line of etch pits was observed at the coalesced boundary. Three types of etch pit shapes were observed. Cross-sectional bright- and dark-field TEM was performed to investigate the correspondence between the etch pits and dislocations. As a result, the majority of etch pits (Type I: 95%, Type II: 3.5%) were found to originate from edge dislocations. Type-III etch pits (1.5%) were not accompanied by dislocations; hence the cause was something else. This technique provides a useful and powerful way to visualize the dislocation distribution in a wide area, which is difficult to explore by TEM.

Acknowledgements

Part of this work was supported by Innovative Science and Technology Initiative for Security (JPJ004596), ATLA, Japan.

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Figure captions

Fig. 1. Bird's-eye view SEM images of α -Ga₂O₃ grown on the striped mask for (a) 15 min, (b) 1 h, and (c) 1.5 h.

Fig. 2. Cross-sectional TEM images of an α -Ga₂O₃ stripe: (a) bright-field image taken under zone-axis condition; and dark-field images with a diffraction vector of (b) $g = \bar{1}\bar{1}20$ and (c) $g = 0006$.

Fig. 3. Bird's-eye view SEM images of coalesced α -Ga₂O₃ films. (a) and (b): As-grown and etched samples grown on the stripe mask with 5- μ m-width windows, respectively. (c) and (d): As-grown and etched samples grown on the stripe mask with 1- μ m-width windows, respectively. Note that horizontal

lines in (c) are charging artifact.

Fig. 4. A magnified plan-view SEM image of the etch pits.

Fig. 5. Cross-sectional TEM images including three Type-I etch pits: (a) a bright-field image taken under zone-axis condition; and the dark field images with a diffraction vector of (b) $g = \bar{1}\bar{1}20$, and (c) $g = 0006$. The arrows show the positions of the pits.

Fig. 6. Cross-sectional TEM images including a Type-I etch pit and two Type-II etch pits: (a) a bright-field image taken under zone-axis condition; and the dark-field images with a diffraction vector of (b) $g = \bar{1}\bar{1}20$, and (c) $g = 0006$. The arrows show the positions of the pits.

Fig. 7. Cross-sectional TEM images including a Type-III etch pit: (a) a bright-field image taken under zone-axis condition; and the dark-field images with a diffraction vector of (b) $g = \bar{1}\bar{1}20$, and (c) $g = 0006$. The arrow shows the position of the pit.