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The analysis of the etch pits parameters in the $(\bar{2}01)$ plane of the β-Ga_2O_3 substrate crystals

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Abstract. Selective wet etching technique was applied to commercial $(\bar{2}01)$ β-Ga_2O_3 single crystal substrates. Some etching recipes allowed us to reveal sharp etch pits on the surface of the substrates. The geometric shape, orientation and density of etch pits were investigated in as-delivered specimens. An observation of mutual location of the etch pits indicates the likely formation low-angle grain boundaries that can form upon heating. Selective wet etching technique was applied to commercial $(\bar{2}01)$ β-Ga_2O_3 single crystal substrates. Some etching recipes allowed us to reveal sharp etch pits on the surface of the substrates. The geometric shape, orientation and density of etch pits were investigated in as-delivered specimens. An observation of mutual location of the etch pits indicates the likely formation low-angle grain boundaries that can form upon heating.

Keywords: selective wet etching, β-Ga_2O_3, gallium oxide, semiconductor, crystal substrate, low-angle grain boundaries

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Introduction

Gallium oxide is a promising ultra-wideband semiconductor that is beginning to find applications in microelectronics [1–3]. Tamura Corporation (Japan) has developed a pilot production of wafers from its own high-quality β-Ga_2O_3 single crystals grown from melt by the edge-defined film-fed crystal growth (EFG) method [4–6]. During the mechanical processing of the grown crystals in order to obtain epi-ready substrates, they acquire various deformation defects. At the moment, there is very little information about defects in the structure of gallium oxide subsurface layers formed as a result of post-growth processing [7-9], however, excepting growth defects are considered more often. At the same time, it is obvious that structural defects in substrates can seriously affect the electrophysical properties of epitaxial structures, that might to be grown on them [10,11]. Therefore, the problem of monitoring and controlling of the substrate defect structure is extremely important.

One of the successfully used approach for studying the defect structure of semiconductor crystals is to involve selective wet etching [12,13]. The necessary detail of this technique is to select the etchant, temperature and duration of the process for a sample to be studied. As a result, the etch pits appear on the etched surface, which may be associated with structural defects of a certain type or a group of them. Hence, it becomes possible to investigate defects

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structure of this material using low-cost express method. Nakai et. al. [14] used this technique to study structural defects in commercial (010) β-Ga_2O_3 bulk single crystals. They revealed etch pits of two types on the surface of the wafers after etching. Using the transmission electron microscopy (TEM), the authors of this paper identified them as screw dislocations on the $(\bar{2}01)$ and (001) surfaces and nanotubes with diameter of 0.1 μm and a length about 15 μm, arranged along the $[\bar{2}01]$ direction. A number of structural defects are present in these *epi-ready* substrates, including those influencing the bulk of the material.

The aim of this work is to study the parameters of etch pits in the $(\bar{2}01)$ β-Ga_2O_3 substrate crystals, at different etching modes.

Materials and methods

We studied the $(\bar{2}01)$ β-Ga_2O_3 substrates that were cut out of the wafers that were grown and post-growth processed (including chemical-mechanical polishing (CMP)) by Tamura Corporation. According to their specification, these wafers have a high crystalline perfection [4].

X-ray diffraction (XRD) measurements were performed at a modified Bourevestnik DRON-7 setup with Cu $K_{\alpha 1}$ (1.5406 Å) irradiation and a Ge (111) monochromator crystal in the two-crystal mode. With its help the crystallographic planes of the substrates were detected.

Selective wet etching was applied to the substrates. Acid and alkaline compositions were used as etchants: H_3PO_4 (82 wt.%) and KOH (45 wt.%), correspondingly. Etching was performed in a Snoll 4/1300 muffle furnace in air.

The sample surface and the geometry of the etch pits were examined using a scanning electron microscope (SEM) Supra 55VP.

Results and discussion

Selective wet etching was performed using the following modes: (EM1) 5 min at 200 °C in H_3PO_4; (EM2) 10 min at 250 °C in H_3PO_4; (EM3) 5 min at 200 °C in KOH; (EM4) 10 min at 200 °C in KOH. The choice of etching modes for bulk gallium oxide in orthophosphoric acid was based on a number of papers [15-19] where etching procedure was applied to commercial $(\bar{2}01)$ Ga_2O_3 wafers. However, our experiment showed that more optimal modes can be reached in the case of increasing the temperature (200 °C instead of 130 °C – 140 °C) and significantly reducing the duration (5 - 10 min instead of 1 - 7 h). The etching modes in alkaline media were selected empirically, since no particular information on the etching modes was found in the publications where etching of $(\bar{2}01)$ Ga_2O_3 by KOH was described. Figure 1 shows SEM images of the sample surfaces that were subjected to the following etching modes: EM1, EM2, EM3, EM4 (Fig. 1(a,b,c,d), correspondingly). The crystal orientation of substrates was determined in advance by XRD. In Fig. 1(a) the elongated etch pits with dimensions of the order-of-magnitude of (700×100) nm (EM1, see Fig.2(a) for details) are displayed. They have a common orientation and the average concentration of $8.5 \cdot 10^5$ cm^{-2}. Similar etch pits, but much larger (15×4 μm) and of much lower density (10^4 cm^{-2}) were observed on the surface $(\bar{2}01)$ of a bulk β-Ga_2O_3 crystal and were classified as *small-pits type* [17]. Other authors established a dislocation nature of these pits using transmission electron microscopy TEM [18]. They found the FWHM value for the $\bar{2}01$ XRD reflection curve to be quite small (17 arcsec), so they associated this fact with a low dislocation density in the bulk β-Ga_2O_3 crystal sample [17].

Etching pits (call them *x-type*) in Fig. 1(b) (EM2, see Fig.2 (b) for details) have elongated coffin-like shape and dimensions of the order-of-magnitude of (25×10) μm, their density is $7.3 \cdot 10^5$ cm^{-2}.

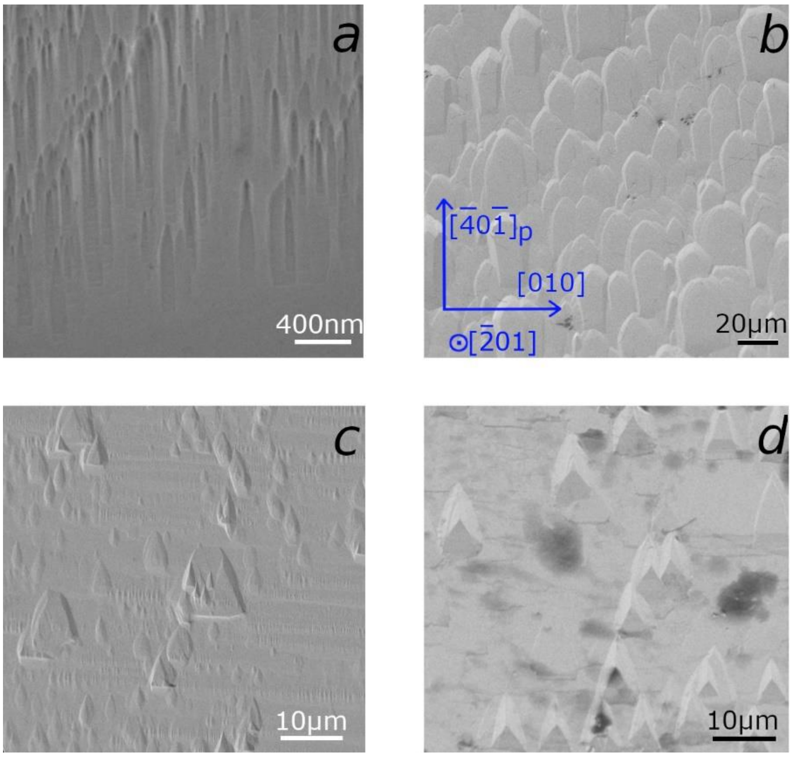

Fig. 1. SEM images of etch pits on the surface of the $(\bar{2}01)$ β-Ga_2O_3 substrates, subjected to etching: *a* – 5 min at 200 °C in H_3PO_4 (EM1 mode), *b* – 10 min at 250 °C in H_3PO_4 (EM2 mode), *c* –5 min at 200 °C in KOH (EM3 mode), *d* – 10 min at 200 °C in KOH (EM4 mode)

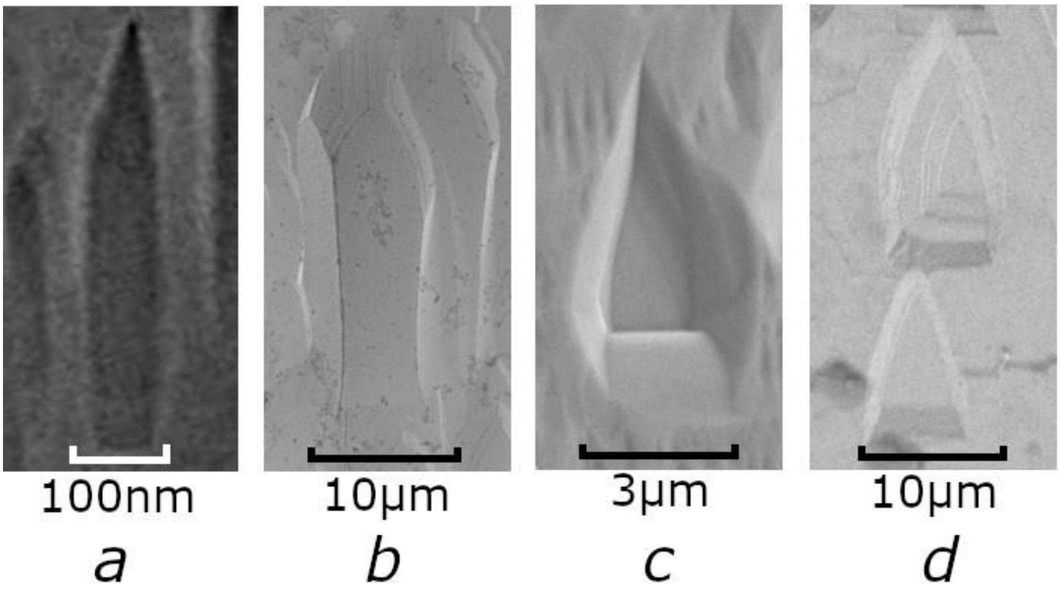

Fig. 2. SEM images of the different types of etch pits on the surface of the $(\bar{2}01)$ β-Ga_2O_3 substrates: *a* – “*small-pits*” pits, *b* – “*x-type*” pits, *c* – *arrow-shaped* pits, *d* – “*y-type*” pits, corresponding to: Fig. 1

In Figures 1(c,d) there are similarly oriented etch pits having the form of triangles (EM3 and EM4, correspondingly, see Fig. 2(c,d) for details, correspondingly), which are also oriented in the same direction with their major axes. Their sizes are of the order of magnitude of (4×3) µm and (10×7) µm, correspondingly. Earlier the pits shown in Fig. 1(c) (Fig. 2(c)) were found by a number of researchers [15-19] and classified in [15] as *arrow-shaped pits type*. These etch pits have an elongated wedge shape, their major axes coinciding with the [102] direction [15]. In [18] this type of etch pits located in the plane $(\bar{2}01)$ is associated with edge dislocations. Their density was estimated [15,18] within the range of $10^4 - 10^5$ cm^{-2}, which is close to one obtained in this work: $7 \cdot 10^5$ cm^{-2}. The pits in Fig. 1(d) (see Fig. 2(d) for details) (call them *y-type*) differ from arrow-shaped ones in having a complex bottom shape.

It should be noted that all the etch pits obtained in this study are oriented similarly; their major axes coincide in direction with the $[\bar{4}0\bar{1}]$ projection onto the surface plane, which is confirmed by the crystallographic orientation detection procedure described above. The analysis of the shape, orientation, and density of small-pits and arrow-shaped ones shows both pit sets to be of the same type, but obtained using different etching modes (with different etchants), which is confirmed in [15] (in comparison with [17]). The *x-type* etch pits in Fig. 2(b) and the *y-type* in Fig. 2(d) correspond to the *small-pits* in Fig. 1(a) and *arrow-shaped pits* in Fig. 2(c), but with longer etching procedures. Thus, all the etch pits obtained in this work represent the same type of defect structures; the difference in their shapes and sizes is due to the etching mode.

In the review [20] a number of authors obtained similar etch pits while studying of Ga_2O_3 bulk crystals. Using TEM, some of them established the dislocation nature of structure defects that initiated such etch pits.

In some regions of the surface of the samples subjected to EM3 mode (Fig. 3) a few chains of etch pits aligned along [010] were observed. Similar ordered linear arrays of etch pits, of the same orientation, were previously obtained by the authors [18] who investigated the structure defects in $(\bar{2}01)$ and (010) Ga_2O_3 single crystal wafers by selective wet etching in orthophosphoric acid. Based on a TEM experiment, they stated that these etch pits were originated by edge dislocations and suggested that the linear arrays of etch pits were formed by ordered groups of dislocations with a possible (101) slip plane.

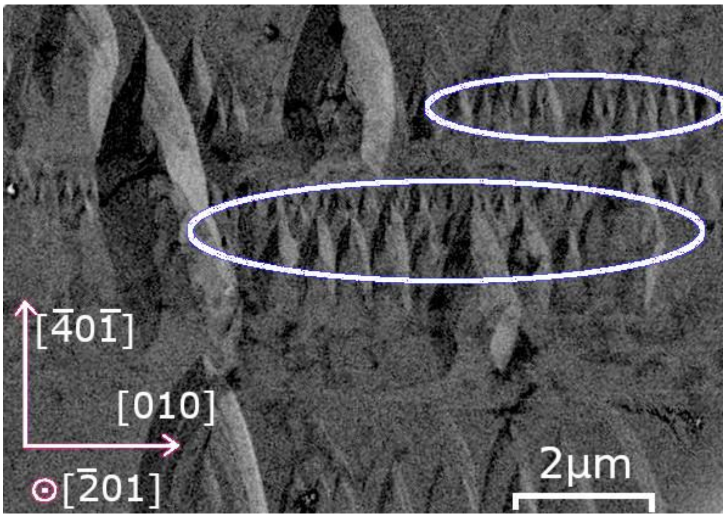

Fig. 3. SEM image of linear arrays of etch pits at the surface of the $(\bar{2}01)$ β-Ga_2O_3 substrates subjected to etching (EM3 mode)

Dislocations distributed over the grains bulk, being defects of regular structure, create stress fields in the occupied volumes and, as a consequence, have energetically unfavorable positions. In case of dislocations acquire energy sufficient for mobilization, they tend to move to regions of lower density – regions of grain boundaries. Then the dislocation density in the grain decreases and the migrated dislocations accumulate in the grain boundaries, forming low-angle boundaries or dislocation walls, which can be displayed as linear arrays of etch pits. A work clarifying this proposition is being prepared.

Conclusion

The effective etching modes for epi-ready ($\bar{2}01$) β-Ga_2O_3 substrates have been developed. The modes that utilize alkali as an etchant were described for the first time. The series of etching procedures using H_3PO_4 were optimized. All the developed modes have reduced process duration and pronounced etch pit geometry. By applying any of these modes it is possible to analyze etch pits parameters, mutual arrangement and density independently.

It was stated, that etch pits are co-directed and coincide parallel to their major axis with [$\bar{4}0\bar{1}$] direction. All obtained etch pits are originated by the same structural defects. The average density of the etch pits of is 7×10^5 cm^{-2}.

The ordering of the arrays of the etch pits along [010] direction takes place upon heating. Based on this, a hypothesis was made, that regularly ordered liner arrays of etch pits might be connected with dislocation groups, forming domain walls with appearance of small-angle boundaries.

References

1. Pearton SJ, Yang J, Cary PH, Ren F, Kim J, Tadjer MJ, Mastro MA. A review of Ga2O3 materials, processing, and devices. *Applied Physics Reviews*. 2018;5(1): 011301.
2. Nikolaev VI, Stepanov SI, Romanov AE, Bougrov VE. 14 - Gallium oxide. In: *Single Crystals of Electronic Materials*. Woodhead Publishing; 2019. p.487–521.
3. Bryushinin MA, Sokolov IA, Pisarev RV, Balbashov AM. Material characterization of a β-Ga2O3 crystal. *Materials Physics and Mechanics.* 2016;27(1): 68-73
4. *Tamura Corporation*. Available from: http://www.tamuracorp.com [Accessed 5th May 2023].
5. Zhang S, Lian X, Ma Y, Liu W, Zhang Y, Xu Y. Growth and characterization of 2-inch high quality β-Ga2O3 single crystals grown by EFG method. *Journal of Semiconductors*. 2018;39(8): 083003.
6. Fu B, Jian G, Mu W, Li Y, Wang H, Jia Z. Crystal growth and design of Sn-doped β-Ga2O3: Morphology, defect and property studies of cylindrical crystal by EFG. *Journal of Alloys and Compounds.* 2022;896: 162830.
7. Gao S, Wu Y, Kang R, Huang H. Nanogrinding induced surface and deformation mechanism of single crystal β-Ga2O3. *Materials Science in Semiconductor Processing*. 2018;79: 165–70.
8. Butenko PN, Guzilova LI, Chikiryaka AV, Boiko ME, Sharkov MD, Almaev AV, Nikolaev VI. Impact on the subsurface layers of the single-crystal β-Ga2O3 wafers induced by a mechanical wear. *Materials Science in Semiconductor Processing*. 2022;143: 106520.
9. Gao P, Tan B, Yang F, Li H, Bian N, Sun X, Wang, R. Influence of diamond wire saw slicing parameters on (010) lattice plane beta-gallium oxide single crystal wafer. *Materials Science in Semiconductor Processing*. 2021;133: 105939.
10. Wu YQ, Gao S, Huang H. The deformation pattern of single crystal β-Ga2O3 under nanoindentation. *Materials Science in Semiconductor Processing*. 2017;71: 321–325.

11. Wu YQ, Gao S, Kang RK, Huang H. Deformation patterns and fracture stress of beta-phase gallium oxide single crystal obtained using compression of micro-pillars. *Journal of Materials Science*. 2018;54(3): 1958–1966.
12. Okumura H, Tanaka T. Dry and wet etching for β-Ga2O3 Schottky barrier diodes with mesa termination. *Japanese Journal of Applied Physics*. 2019;58(12): 120902.
13. Ohba E, Kobayashi T, Kado M, Hoshikawa K. Defect characterization of β-Ga2O3 single crystals grown by vertical Bridgman method. *Japanese Journal of Applied Physics*. 2016;55(12): 1202BF.
14. Nakai K, Nagai T, Noami K, Futagi T. Characterization of defects in β-Ga2O3 single crystals. *Japanese Journal of Applied Physics*. 2015;54(5): 051103.
15. Kasu M, Oshima T, Hanada K, Moribayashi T, Hashiguchi A, Oishi T, Ueda O. Crystal defects observed by the etch-pit method and their effects on Schottky-barrier-diode characteristics on (201) β-Ga2O3. *Japanese Journal of Applied Physics*. 2017;56(9):091101.
16. Oshima T, Okuno T, Arai N, Kobayashi Y, Fujita S. Etching of β-Ga2O3 Substrates. *Japanese Journal of Applied Physics*. 2009;48(4): 040208.
17. Kuramata A, Koshi K, Watanabe S, Yamaoka Y, Masui T, Yamakoshi S. High-quality β-Ga2O3 single crystals grown by edge-defined film-fed growth. *Japanese Journal of Applied Physics*. 2016;55(12): 1202A2.
18. Ueda O, Ikenaga N, Koshi K, Iizuka K, Kuramata A, Hanada K, Kasu, M. Structural evaluation of defects in β-Ga2O3 single crystals grown by edge-defined film-fed growth process. *Japanese Journal of Applied Physics*. 2016;55(12): 1202BD.
19. Hanada K, Moribayashi T, Koshi K, Sasaki K, Kuramata A, Ueda O, Kasu M. Origins of etch pits in β-Ga2O3(010) single crystals. *Japanese Journal of Applied Physics*. 2016;55(12): 1202BG.
20. Fu B, Jia Z, Mu W, Yin Y, Zhang J, Tao X. A review of β-Ga2O3 single crystal defects, their effects on device performance and their formation mechanism. *Journal of Semiconductors*. 2019;40(1): 011804.

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