Inversion Boundaries Developed by Etching on $\{10\bar{1}0\}$ of ZnO Crystal*

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Abstract

Etch pattern on surfaces of ZnO crystal has been observed by using an E.M. and an S.E.M. Two kinds of boundaries on which stacking orders of Zn and O atomic planes change have been developed on the plane $\{10\bar{1}0\}$ by using etching technique. Hydrofluoric acid (~46%) was used as etchant. One boundary on which stacking of Zn and O planes changes from one order, -O.Zn-O.Zn-, to the other order, -Zn.O-Zn.O-, is a twin boundary. While, the other boundary on which stacking of Zn and O planes changes from the latter order to the former one is not considered as a twin one. Results of observation suggest to us that the decrease in the growth rate of the crystal needle is due to the generation of twin boundaries in the crystal.

§1. Introduction

Polarity of ZnO crystal has been studied by the several authors. From the result of X-ray analysis, Mariano *et al.* have confirmed that in ZnO crystal, polarity of the spicular growth end as grown is electropositive[1]. From the result of chemical etching study using Hydrofluoric acid, Klein has assigned the positive sign of the c-axis of the crystal to the direction of the vertexes of pseudo-isosceles triangles, etch figure, produced on the plane $\{10\bar{1}0\}$[2]. He also reported the etch figure as hillock. By chemical etching study, Heiland *et al.* have found that ZnO crystal grows sometimes as the one which is divided into two parts. One is the central lod and the other is

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a cylinder surrounding the first one. These two parts in the crystal have a coaxis along the c-axis, and the opposite directions in polarity[3]. According to ion bombardment experiment performed by ourselves, the atomic plane on the spicular growth end has been confirmed as a Zn plane. On the other hand, it was found to be ambiguous that the plane on the flat growth end is a Zn plane or an O plane. We, therefore, suggested that ZnO crystal might grow in stacking orders of Zn and O planes as not only one order, -Zn.O-Zn.O- but also the other order, -O.Zn-O.Zn-[4]. Gehman *et al.* have reported that interstice lattice stacking faults in the structure such as BeO bicrystal lead to the formation of inversion twins, as shown in his schematic model of the structure of the crystal[5]. By chemical etching study, we have found two kinds of boundaries on which stacking orders of Zn and O planes change along the c-axis[6].[7]. In the present paper, the experimental results obtained by ourselves are reported in detail.

§ 2. Observation

ZnO crystal needles (1 mm squares in cross section and 10 mm in length) were prepared by our method. That is, needles were prepared by heating ZnF_2 in air at elevated temperatures[8]. Then, the needles were etched by Hydrofluoric acid (~46%) for 20 min in room temperature.

A. $\{10\bar{1}0\}$ plane

The chemical etching behaviors on the planes $\{10\bar{1}0\}$ are as follows: In the crystal with the spicular growth end, the etch feature as shown in Fig. 1 is similar to the pattern, pseudo-isosceles triangle, in agreement with Klein's observation.[2] The pattern was confirmed as pits by stereographs. The pattern on the etched crystal with the flat growth end is shown in Fig. 2(a). In the figure, a fine line is observed. It is seen that the line shown in Fig. 2(b) which corresponds to the fine line mentioned above, is perpendicular to the c-axis. In Fig.2(a), besides the line, another curved boundary is also observed in the upper region. Fine lines and curved boundaries are, hereafter, referred as F-boundary and C-one, respectively. The direction of pseudo-isosceles triangles in the two regions separated by F-boundary or C-one are all the same in each region. Triangles in the regions separated by boundaries are face to face with their vertexes, and face to face with their bases on F-boundary and on C-one, respectively. In Fig. 3, it is observed that two regions separated by F-boundary do not show misfit, that is in coherent, on the boundary. On the other hand, in Fig. 4, it is observed that those two regions separated by C-boundary show misfit, that is in incohernt. The stereographs as shown in Fig. 5 (a) and (b) show that F-boundary is a fine protrusive band and that C-boundary exists in rather depressed zone.

B. {0001} plane

Fig. 6 (a) and (b) show the etch patterns developed on the planes {0001} and {10$\bar{1}$0} of a couple of crystals which had been obtained by cleaving a crystal needle rather perpendicularly to the c-axis. In these figures, it is seen that two surfaces {0001} which are different in polarity suffer diffrent effects by etching. Sometimes two groups of vertexes and bases of pseudo-isosceles triangles are observed on the intersection of the planes {0001} and {10$\bar{1}$0}. Such a crystal is referred as *S* crystal. An example of the irregular pattern on the etched surface of *S* crystal is shown in Fig. 7. In the figure, it is observed that rough and smooth regions have been developed on a etched surface. It is seen that the former had been etched more easily than the latter which is the background of a few number of larger conical pits.

§ 3. Discussion

Klein has assigned the positive sign of the c-axis of the crystal to the direction of the vertex of pseudo-isosceles triangle produced on the plane {10$\bar{1}$0} of ZnO crystal[2]. Heiland *et al.* have reported that the direction of the positive sign of the c-axis coincides with Zn atomic plane which is the polarized surface of ZnO crystal[3]. From these and the etch pattern on the plane {10$\bar{1}$0} as shown in Fig. 2, it can be clearly concluded that there are two kinds of inversion boundaries and that stacking orders of Zn atomic plane and O one are opposite to each other in each region separated by F-boundary and C-one. In other words, stacking of Zn and O planes changes from one order, -O.Zn-O.Zn-, to the other order, -Zn.O-Zn.O-, on F-boundary and changes from one order, -Zn.O-Zn.O-, to the other order, -O.Zn-O.Zn-, on C-one. The plane {10$\bar{1}$0} is etched such that F-boundary behaves as a protrusive band and C-one exists in a depressed zone. This fact means that C-boundary is etched more easily than F-boundary. From these, the schematic top view of the etched plane {10$\bar{1}$0} can be drawn as shown in Fig. 8 (a) and (c). As shown in these figures, $l'_1 < l'_2$, where l'_1 and l'_2 show thickness of crystal layers which had been etched out of the surface planes {1010}. Mariano *et al.* have confirmed that negatively polarized O atomic planes is etched more easily than positivey polarized Zn atomic planes[1]. The figures shown in Fig. 6 (a) and (b) coincide with their confirmation.

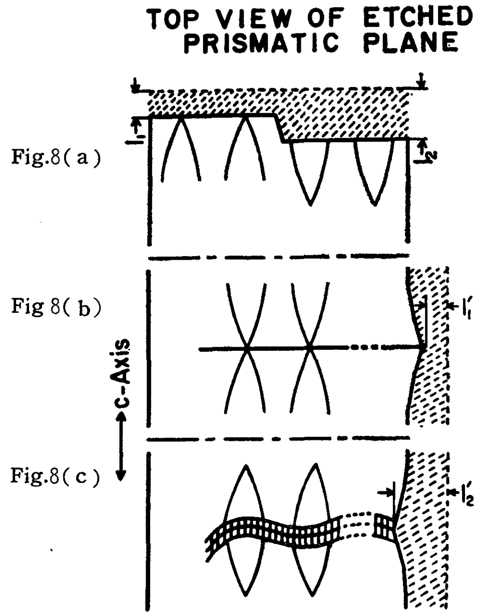

Fig.8(a). The schematic representation of the etched surface {0001}. In the figure, $l_1 < l_2$, where l_1 and l_2 represent thickness of crystal layers which had been etched out of the polarized Zn planes and O ones, respectively.

Fig.8(b) and (c). The schematic representation of the etched $\{10\bar{1}0\}$. In these figures, $l'_1 < l'_2$, where l'_1 and l'_2 represent thickness of crystal layers which had been etched out of the surface planes $\{10\bar{1}0\}$.

From these, and the etch pattern on {0001} shown in Fig.7, a schematic top view of the etched planes $\{10\bar{1}0\}$ of *S* crystal can be drawn as shown in Fig. 8 (a). As shown in the figure, $l_1 < l_2$, where l_1 and l_2 show thickness of crystal layers which had been etched out of polarized Zn planes and O ones, respectively. Gehman *et al.* have reported that interstice lattice stacking faults in the structure such as BeO bicrystal lead to the formation of twins[5]. They have also suggested a model to explain the character of the crystal, wurtzeite type. The model is shown schematicalley in Fig. 9. In the figure, full lines and dotted ones represent closed packed anion layers and cation ones, respectively. Of course, anion and cation correspond to O and Be ions, respectively. Two kinds of distances between an O atomic plane and a Be atomic one are 1.659±0.003Å and 1.645±0.003Å. When an O atomic plane is the crystal surface, the surface is polarized electronegatively.

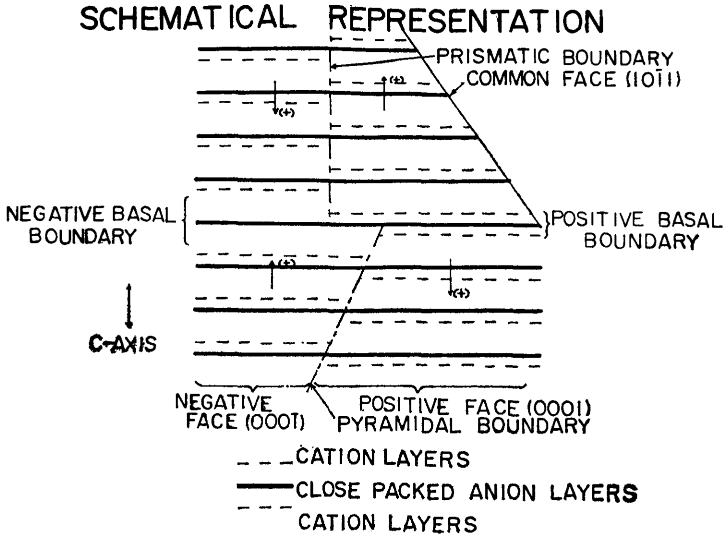

Fig.9. A schematical representation of the structure of BeO crystal. This model had been suggested by Gehman *et al.*

Furthermore, Gehman *et al.* appointed that there are two kinds of twin boundaries as shown in Fig. 9. One twin boundary corresponds to the inversion boundary on where the stacking order of Be and O changes from one order, -O.Be-O.Be-, to the other order, -Be.O-Be.O-. The other twin boundary corresponds to the inversion boundary where the stacking order changes from one order, -Be.O-Be.O-, to the other order, -O.Be-O.Be-. The former boundary is negative basal one which is in lack of Be atomic plane, while, the latter one is positive basal one which is in excess of Be atomic plane. Gehman *et al.* has assumed that the O sublattice is continuous across the twin boundary, and that the discontinuity exists only in the Be sublattice.

If the model of the crystal structure of BeO is possible to apply to the crystal structure of ZnO which is also II-VI compound as BeO, F-boundary and C-one in ZnO crystal should correspond to the negative and positive basal boundaries, respectively. Of course O surface and Zn one of the crystal are also negative and positive, respectively. Two schematic etch patterns shown in Fig. 8 (a) and (c) are in inconsistent with the ones which should deducted from Gehman *et al.*'s model. From the fact C-boundary intersects obliquely with the c-axis, it can be considered that no C-boundary corresponds to the one type of the twins suggested by Gehman *et al.* In preparation of ZnO crystal by using our method, both kinds of crystals with the spicular growth ends and the ones with the flat growth ends had been sometimes produced on the inside wall of platinum crucible. The length were larger in the former than in the latter. No C-boundary has developed on the etched planes $\{10\bar{1}0\}$

of the former but on the etched planes $\{10\bar{1}0\}$ of the latter. These facts suggest to us that the decrease in the growth rate of ZnO crystal inside the platinum crucible is due to the generation of F-boundary caused by any change in the crystal growth conditions in the growing stage. It is clear that after the generation of F-boundary, the stacking order of Zn and O changes from one order, -O.Zn-O.Zn-, to the other order, -Zn.O-Zn.O-, therefore, O plane becomes the new growth front.

F-boundary is a straight line which is perpendicular to the c-axis and C-boundary zigzagged. These facts suggest to us that the terminal plane, Zn plane, of the stacking order, -O.Zn-O.Zn-, and the starting plane, Zn plane, of the order, -Zn.O-Zn.O- is joined more easily than the terminal plane, O plane, of the stacking order, -Zn.O-Zn.O-, and the starting plane, O plane, of the order, -O.Zn-O.Zn- does. Stepped O planes may play a role of a substrate on which newly created ZnO molecules contact in the stacking order, -O.Zn-O.Zn- to make an apparent misfit between the terminal O plane in the order, -Zn.O-Zn.O-, and the starting O plane in the order, -Zn.O-Zn.O-.

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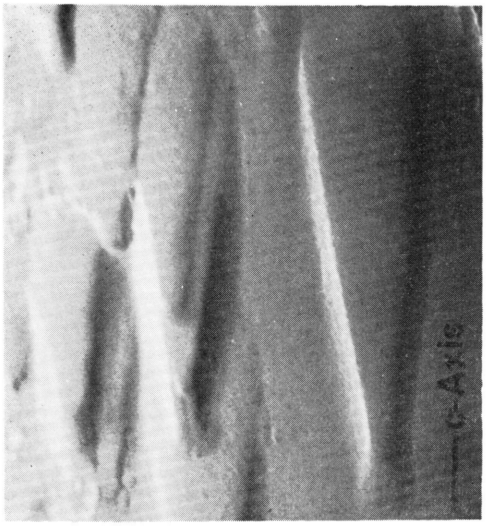

Fig.1 $\times 1,000$

Etch pits, pseudo-isosceles triangles, developed on the plane $\{10\bar{1}0\}$.

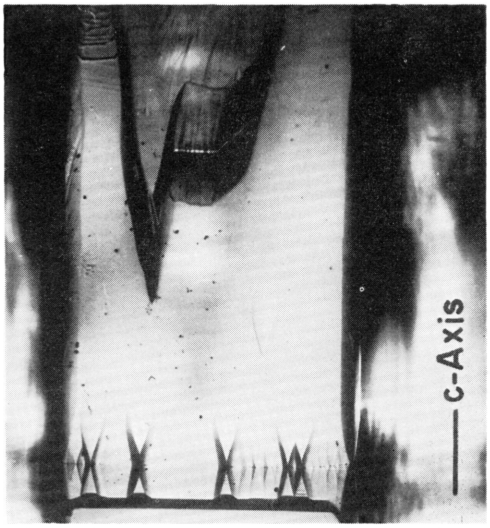

Fig.2 (a) $\times 150$

Two kinds of inversion boundaries developed on the plane $\{10\bar{1}0\}$ by etching. Boundaries are observed in the upper and the lower regions.

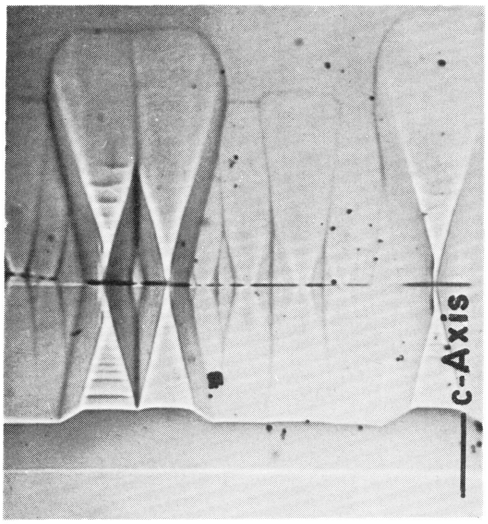

Fig.2 (b) $\times 400$

The enlarged pattern around the boundary corresponding to the one, shown in the lower region in Fig.2 (a).

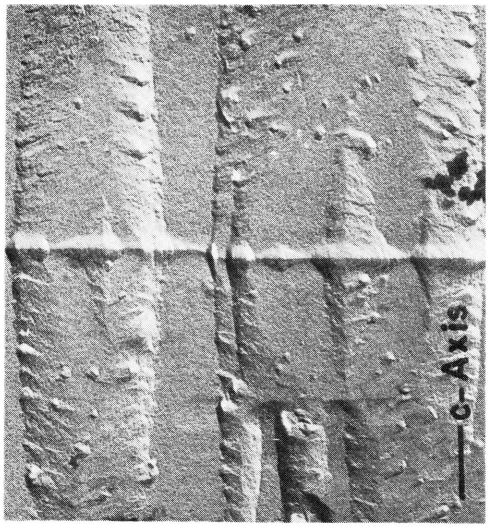

Fig.3 ×10,000

Two regions separated by F-boundary. They are in coherent to each other on the boundary.

Fig.4 ×10,000

Two regions separated by C-boundary They are in incoherent to each other on the boundary.

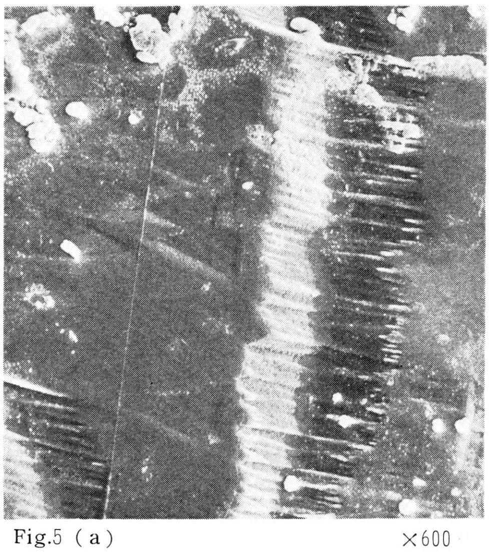

Fig.5 (a) ×600

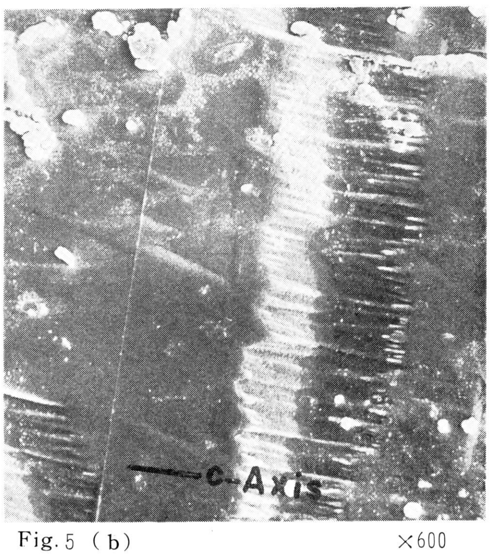

Fig. 5 (b) ×600

A couple of stereographs which show the same regions including F- and C-boundaries. The figures show that F boundary is protrusive band and C-one exists in rather depressed zone.

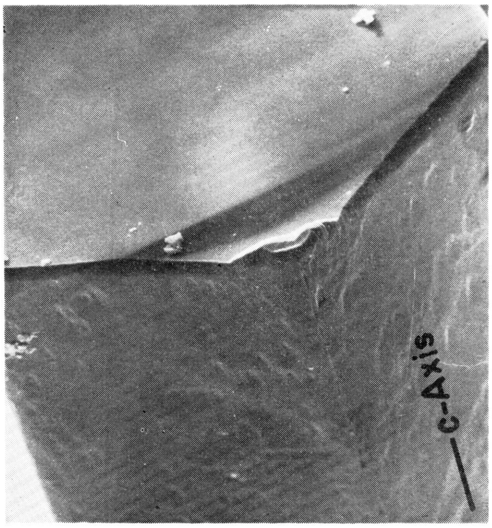

Fig.6 (a) ×300

The figures in the lower region and the upper one are the etch patterns on the planes {10$\bar{1}$0} and {0001}, Zn atomic plane, respectively.

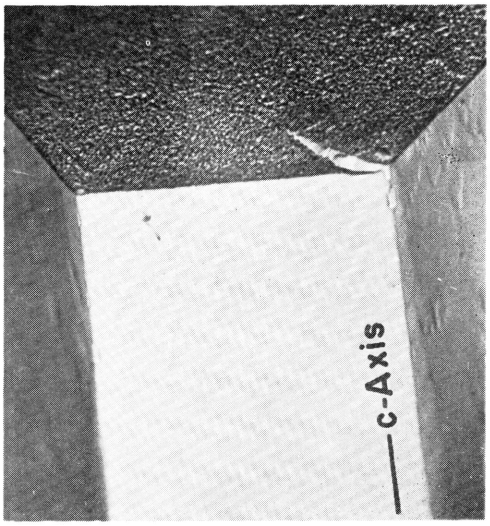

Fig.6 (b) ×300

The figures in the lower region and the upper one are the etch patterns on the planes {10$\bar{1}$0}, and {0001}, O atomic plane, respectively.

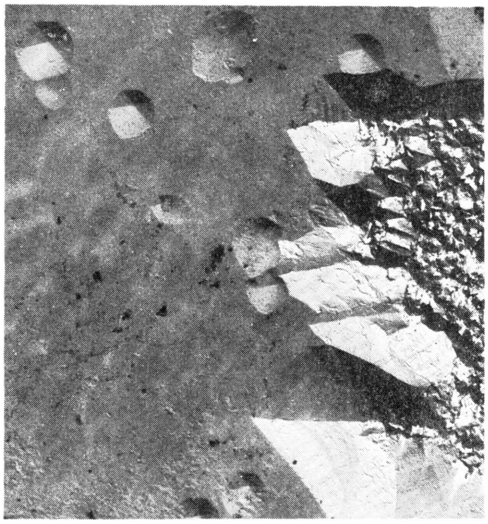

Fig.7 ×1,000

Etching behavior of the surface {0001} which includes different kinds or polarized surfaces. It is observed that rough region is etched more easily than the smooth region which is the background of a few number of larger conical pits.