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Lineage structure formation in lithium niobate

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Several fine lines appeared on the surface of $LiNbO_3$ single crystals grown perpendicularly to the (112) plane from the melt. They ran approximately parallel to the pulling axis from the middle of the cylindrical wall to the tail without terminating in the boules. X-ray analysis showed them to be a lineage structure with a large rotation of the crystallographic axis around the pulling axis and with small tilted orientations perpendicular to the pulling axis. The structure initiates on the lateral surface during crystal growth and is dependent on the growth direction and the crystal diameter. It is stable the finding that the structure does not reform when annealed at 1150°C. Transfiguration of growth ridges by the lineage structure and the solid-liquid interface is flat imply that the lineage structure occurs during crystal growth. The structure forms from nuclei occur on the lateral surface of the crystals and they can develop under crystal growth conditions that produce a convex solid/liquid interface towards the liquid. The nuclei result from changes in the surface in response to surface stress.

1. Introduction

Lineage structures [1–4] have been frequently observed in single crystals grown from the melt. The lineage structures must be defined for all subgrains whose orientations descend continuously from the same parent nucleus in distinction from a low-angle tilted boundary. This substructure is not a serious problem in the routine production of crystals with a large diameter. In fact, crystalline perfection can be achieved by selecting the seeds' orientation such that the growth is not hindered by seeds' orientation other than in the growth direction close to where the lineage structure appears [5]. It has dislocations on its boundaries and is associated with the formation of a polygonized wall [6]. Common dislocation-free semiconductor crystals can be grown from the melt by the neck technique [7]. Since dislocations in single crystals are usually caused by thermal stress, and because the number of lineage structures is small when the dislocation density is lower than $10^3/cm^2$, the crystals should be grown slowly thus avoiding high thermal gradients [8]. Nevertheless, the nature of the lineage structure has not been fully elucidated.

Kuroda and Ookawa [9] showed theoretically that, just after solidification a crystal has a three dimensional network of dislocations and that solid state transformation of the unstable crystal gives rise to lineage structural boundaries. Their model assumes that polygonization needs an excess density of unpaired edge dislocations which can arise from defects grown-in from the melt. Subsequent investigations showed that the rotation axes of mutually misoriented lineage structures lie close to the growth direction [10]. The dislocations on its boundaries would be expected to set the Burgers vector and the slip plane, perpendicular and parallel to the axis, respectively. Thus, the formation could not be explained by simply the restoration of the crystallographic orientation.

This paper deals with the lineage structure of $LiNbO_3$ single crystals grown from the melt. The aim is to investigate the relation between the generation of these defects and the conditions of crystal growth such as the temperature gradient, the seed orientation and the crystal diameter. A mechanism for the formation for the lineage structure will be discussed to explain the experimental results.

2. Experimental procedure

2.1. Crystal preparation

The crystals were grown using an rf-heated Czochralski puller. A platinum crucible 160 mm in diameter and 160 mm in height was imbedded in a granular ZrO_2 thermal insulator contained in an Al_2O_3 crucible. Three different types of furnaces were designed to control the temperature gradient, as shown in Fig. 1. For a high gradient above the melt, a platinum ring with eaves was placed over the platinum crucible (Fig. 1a). The eaves reflected the radiation and cut off the heat flow from the surface of the melt to the upper part of the furnace near the crucible wall. For a low gradient, a cylindrical after-heat furnace had the same diameter as the platinum crucible, to ensure that the heat flow from the melt and the crucible wall to the open structure above the crucible were increased (Fig. 1c). For a mid range temperature gradient, a small after-heater 120 mm in diameter without the platinum ring with eaves was used (Fig. 1b). The temperature gradients in the axial and radial

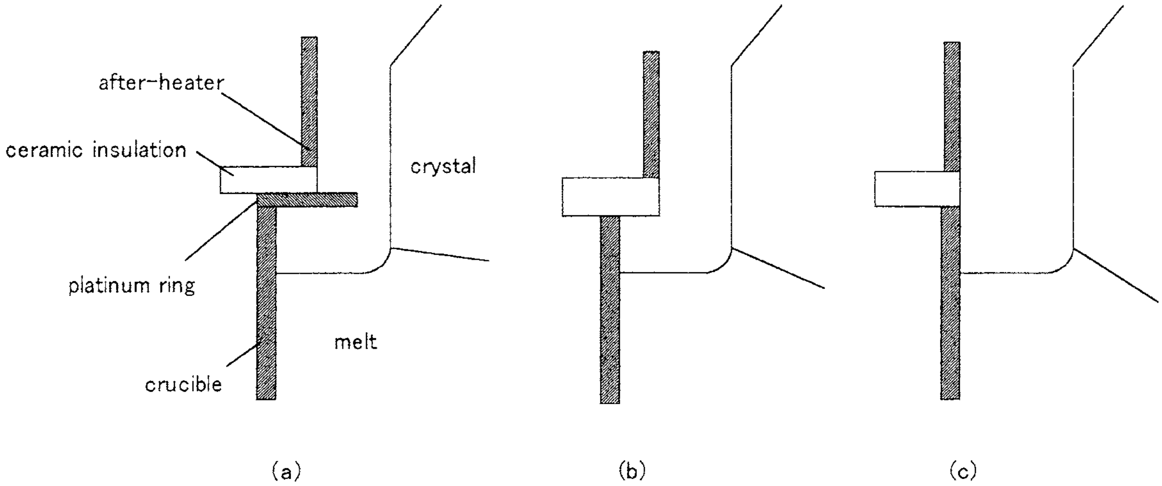


Figure 1 Arrangements around the interface of the solid and liquid in three furnaces of difference types designed to give: (a) high, (b) mid-range, and (c) low temperature gradient.

directions above the melt were $(dT/dZ)_{0-40\,\mathrm{mm}} = 19$, 6 and 5°C/cm, and $(dT/dr)_{0-40\,\mathrm{mm}} = 5$, 3 and 0°C/cm, respectively, of the high, low and mid-range furnaces without the crystal. Temperature measurements were made using a Pt/Pt-Rh13% thermocouple.

The starting material was prepared by mixing Li_2CO_3 (99.99%) and Nb_2O_5 (99.99%) in the proportion required to give a congruent melt [11] and heated at 1100°C for 14 h to form $LiNbO_3$. The melt charge occupied about 90% of the platinum crucible. All of the crystals were grown in air.

The pulling directions were normal to the (112), $(1\bar{1}0)$, $(11\bar{2})$, (111), and (110) planes of the rhombohedral unit cell of $LiNbO_3$. The seeds were made on the single crystals free of cracks, inclusions, prominent low-angle grain boundaries and lineage structure. Because the shape of the interface is influenced by thermal convection and the level of the melt in the crucible, to obtain a flat interface, the crystal rotation and the pulling rate were decreased gradually from 15 to 12 rpm and 6 to 4 mm/h, respectively. Also, to obtain a convex interface, both parameters were kept at 12 rpm and 4 mm/h, even when the shape varied slightly.

2.2. Observations and measurements

Specimens 0.5 mm in thickness were sliced and polished using standard and techniques observed using transmitted light, after marking the boules ferroelectrically single domained. Poling was accomplished in a DC electric field while cooling the boule from 1200 to 1050°C in the furnace.

After mechano-chemical polishing to remove the damaged surface caused by cutting, the crystals were etched with a mixture of HF:HNO_3 (=2:1) for 40 min at about 80°C to reveal the lineage structure.

X-ray traverse topographies of the lineage structure were taken with a conventional Lang camera. The $(1\bar{1}0)$ reflection of Mo K_α radiation was used X-ray diffraction analyses of polished samples were also performed. The back-reflection Laue method was used to measure the variation in angle about the crystal axis or the growth direction at its boundaries. The values were calculated from the distorted or split spots in a photograph of the boundary region. For the misoriented crystal axes about the perpendicular to the pulling axis, the tilted angles were measured from the shift in the peak position in which the separated profiles of the α_1 peaks were recorded by X-ray diffraction. The Cu K_{α_1} source supply was 40 kV and 20 mA. The X-ray beam was diffracted at the boudary; masking by Pb films was employed to illuminate the boundary accurately. The trapping impurities at the boundaries were measured by electron probe micro analysis (EPMA).

3. Results and discussion

3.1. Lineage structure observed in $LiNbO_3$

Several fine lines were often observed directly on the surface of $LiNbO_3$ single crystals running approximately parallel to the pulling axis from the middle of the cylindrical wall to the tail without termination in the boules. The number of the lines increased towards the tail. In contrast, no lines were found in the conical part of the crystals. The lines were formed only when the growth direction was normal to the (112) plane; they were never found when the growth direction was normal to the $(1\bar{1}0)$, $(11\bar{2})$, (111), or (110) planes.

Using polarized light, subgrains were observed deeper in cross sections containing lines, as shown in Figs 2 and 4a. These defects, which were about 0.5 to 1.0 mm in width and 10 or 20 to 40 mm or more in length, were nearly parallel. The extinction taken by the rotation around the normal to the wafer showed that the crystallographic orientation of the subgrains is slightly different from that of the rest of the crystal. The contrast and the area of the subgrains increased towards the tail of the boules, indicating that the misorientations increase. This result is consistent with the observation on the surface of the boules.

Next, when the chemical etching was performed, two etch pits at the junction of the subgrain and several lines bridged across the band were observed as shown in Fig. 3. The subgrains consist of small blocks with their orientation gradually changing so that the grains near the center were aligned with the normal of the wafer and

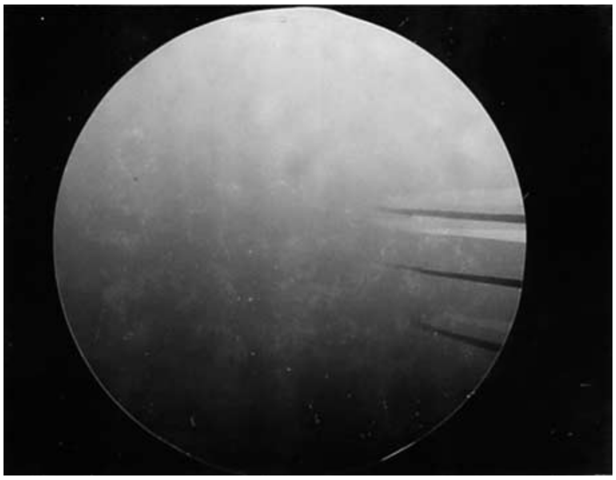


Figure 2 Polarized light was to show slightly rotated subgrains in a cross-section of a $LiNbO_3$ single crystal 3-inches in diameter, they are the stripes on the surfaces of cylindrical part.

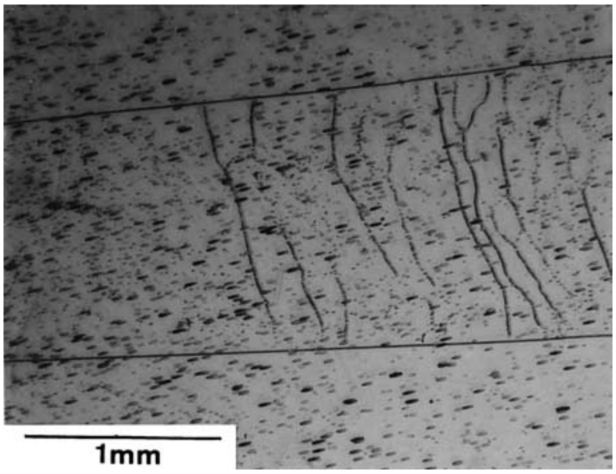


Figure 3 Two lines of etched pits nearly parallel to each other at a junction of the subgrain and the rest of crystal along the $\langle 11\bar{1}\rangle$ direction and several lines bridging across the subgrain.

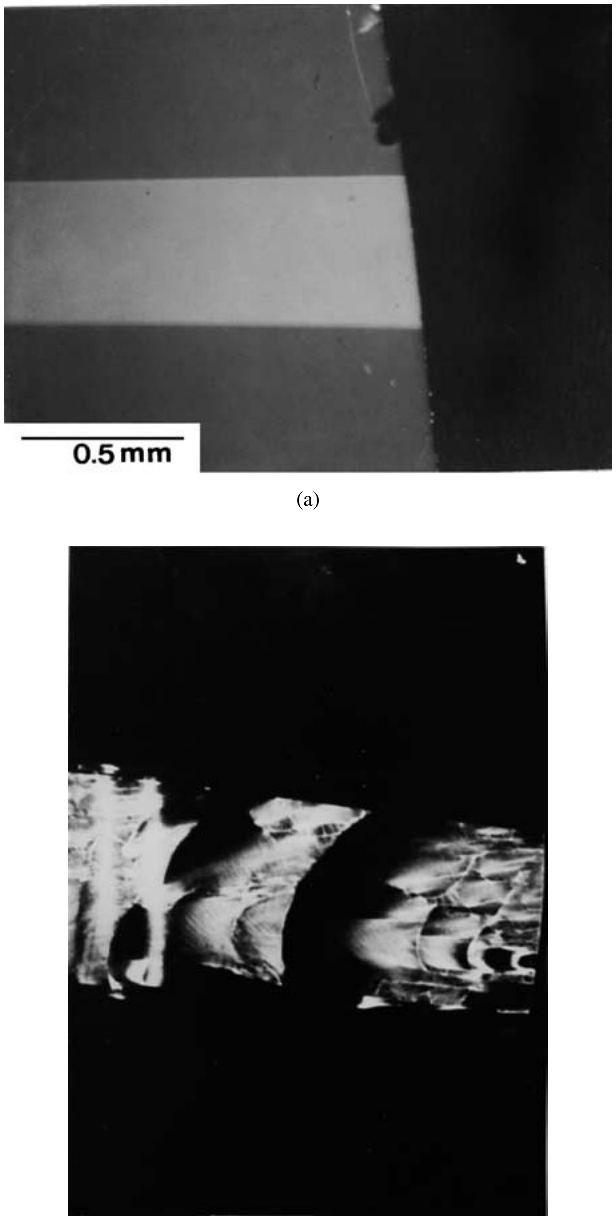
thus not distinguishable. No impurities were detected at the boundaries by EPMA. Lange X-ray diffraction topography showed that the subgrain was a mosaic with small angular mutually oriented blocks as shown in Fig. 4b.

The Laue patterns taken at the boundary region between the subgrain and the matrix had split spots, implying that the subgrain is slightly rotated around the pulling axis. The rotational angle θ was about 0.5° at the edge of the wafer. The rotational angle of the subgrains decreased along the $\langle 11\bar{1}\rangle$ direction towards the center of the crystal as shown in Fig. 5.

Furthermore, from the shift in Bragg angles, the tilted angles were measured about 0.07° for α and about 0.09° for β. Thus, the subgrains can be identified as a lineage structure with a large rotation of the crystallographic axis around the pulling axis and a small titled orientation about the perpendicular to the pulling axis.

3.2. Generation during crystal growth

The lineage structure formed during the ridge growth [12], resulted in discontinued striations and separated



(a)

(b)

Figure 4 Direct images of the subgrain observed: (a) under polarized light and (b) by a conventional Lange X-ray diffraction topography.

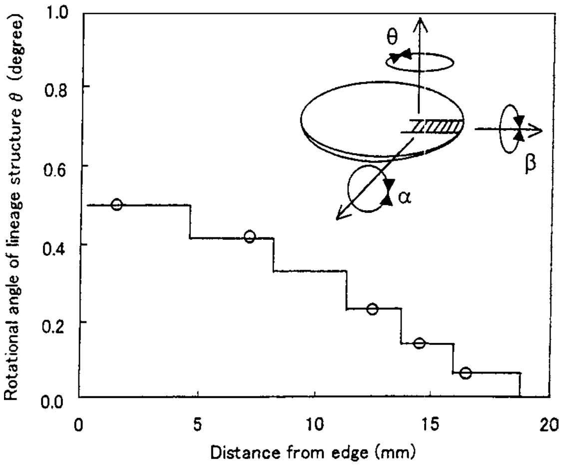


Figure 5 Rotational angle θ around the pulling direction for the misorientation of the crystal axis decreases as the position in the subgrain approaches the center of the crystal. Solid lines indicate that smaller blocks with their orientation gradually changing, to align with the normal of the wafer.

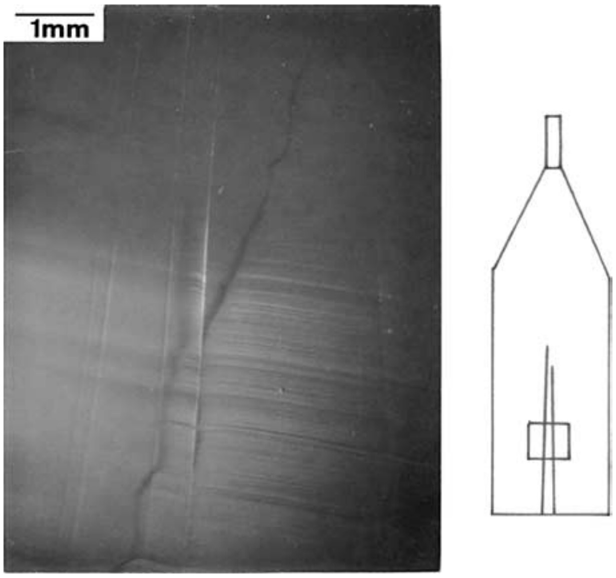


Figure 6 Several fine lines are directly observed on the surface of the cylindrical crystal. They overlie the ridge growth and appear as discontinued striations and separated ridges.

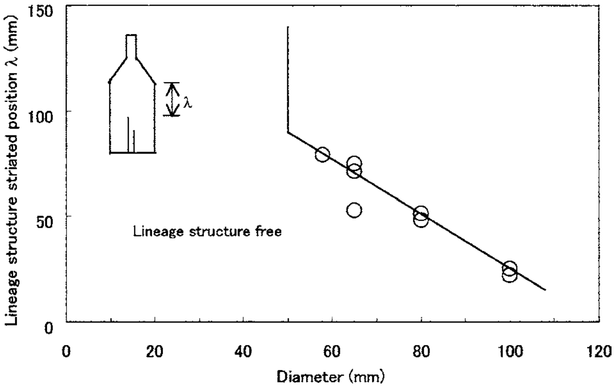


Figure 7 Dependence of the generation of lineage structure on the diameter of $LiNbO_3$ crystal in the range between 50 and 100 mm. No lineage structure can be observed for crystals with a diameter less than 50 mm.

ridges on the surface in Fig. 6. The X-ray diffraction topography indicated that the nucleus of the disorder would burst just upon the surface of the cylindrical crystal and then the disorder would propagate towards the inside of the crystal. The lineage structure starts on the lateral surface during the crystal growth and would be slightly divergent. These defects were stable in the annealing test at 1150°C for 40 h in air. On the other hand, high quality crystals can be grown without lineage structure provided the interface of solid and liquid is kept flat during the growth, even if the growth direction is normal to the (112) plane. A convex interface of the solid in the melt strongly promotes its formation.

A deeper understanding will require investigation of the relation between the crystal diameter and the lineage structure. The position of the structure was determined by measuring the distance λ between the end of the conical part and the line pattern associated with lineages on the cylindrical part of the crystal. The lineage structure was never observed in $LiNbO_3$ smaller than 50 mm in diameter, even if the interface of the solid and liquid was convex. With increasing crystal diameter, the lineage structure formed more easily just below the cone of crystals as shown in Fig. 7. All $LiNbO_3$ single crystals 80 mm in diameter grown under different vertical and radial temperature gradients had a lineage structure which started at $\lambda = 40$–50 mm. However, the size of these defects decreased, as the temperature gradient became smaller. Thus, the generation of the lineage structure is slightly influenced by the temperature gradient in the furnaces.

It should be noted that generation of the nuclei depend on the growth direction and the crystal diameter, and that they can be developed under growth conditions which produce a convex interface between the solid and liquid. This opposes the model of the formation after solidification. Disregarding the effects of thermal stress due to a high temperature gradient, the above results may be explained as the nuclei occurring on the surface of large diameter crystals under any temperature gradients grow strongly by high supercooling when a convex interface between the solid and the melt is formed by a low rotation and a high temperature gradient. High supercooling may occur near the interface in the melt under such crystal growth conditions because the convex interface is exposed to a much colder melt which produces cooling effects due to the melt convection giving weak stirring in the crucible and the enormous heat transfer toward the upper part of the crystal.

3.3. Mechanism of lineage structure formation

On the basis of the surface stress resulting in morphological features on the surface of the crystal during growth, a mechanism for generation of the lineage structure is proposed. The lateral surface atoms just above the meniscus of the melt are arranged differently from how they would if they were at a growth front. On the surface of the crystals, stress forces them out of the positions that they would otherwise occupy. The origin of the lineage structure lies in understanding the spontaneous rotation of the lattice in an attempt to relax the surface stress during the plastic deformation with the regular arrangement of dislocations. The excess free energy is decreased when a part of the surface rotates to put a singular surface with lower free surface energy into the contour, so that a stable structure can be formed if the elastic energy concentrated on the lineage structure is lower. Thus, in the distorted lattice, the nucleus of the lineage structure is attributed to the rotation of the plane of a singular surface around the pulling axis just on the surface of the cylindrical crystals and can propagate towards the inside of the crystal. This behavior is necessary because the plane as a singular surface must stay nearly parallel to the pulling axis. As the diameter of the crystals is increased, the surface stress becomes so large that the lineage structure cannot be avoided. In the case of a flat interface, the surface stress is the lowest because the surface free energy is minimal. Furthermore, the appearance of the singular surface like a facet may be suppressed on the side at a growth front to eliminate lateral growth, because the phases are almost in equilibrium.

When the pulling axis is chosen normal to the (112) plane of $LiNbO_3$, the presence of the (110) plane as the singular surface can reduce the stress resulting from the rotation of the (110) plane. The other directions have no singular surface parallel to the pulling axis, so the lineage structure cannot occur.

4. Summary

Lineage structures were observed in $LiNbO_3$ crystals, grown from the melt, only when the growth direction was normal to the (112) plane. The structures were identified as subgrains with a large rotation of the crystallographic axis around the pulling axis and a small tilted orientation about the perpendicular to the pulling axis. The lineage structure is dependent on the growth direction and the crystal diameter and initiates on the lateral surface during crystal growth. It is stable on annealing at 1150°C. High quality crystals can be grown without the lineage structure when the interface between the solid and liquid is kept flat during the growth, even if the growth direction is normal to the (112) plane. The nuclei of the lineage structure form when the surface of the structure alters during crystal growth in an attempt to reduce surface stress.

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