Effect of Hydroxyl Content on Thermally Induced Change in Surface Morphology of Lithium Niobate (000$\bar{1}$) Substrates

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Two types of LiNbO$_3$ (000$\bar{1}$) single-crystal substrates (LN), a conventional LN containing >10^{19} cm^{-3} OH ions, and a dehydrated LN were annealed in a dry O$_2$ atmosphere, and their surface morphologies were investigated using atomic force microscopy. For the conventional LN with more OH ions, the surface was significantly roughened in the temperature range of 600°-800°C, accompanied by a large outward diffusion of OH, and then it evolved to a steplike morphology at higher temperatures. However, the dehydrated LN surface changed gradually at temperatures of > 700°C to flat terraces without any roughening process. The step heights of the annealed surfaces corresponded to $n/6$ (where n is an integer) of the c-axis length of the LN crystal. The dehydrated LN substrate, along with the dry-annealing process, achieved fairly flat surfaces.

I. Introduction

FERROELECTRIC LiNbO$_3$ (LN) single-crystal substrates have been widely applied in the fabrication of various optical waveguide devices, such as optical modulators.[1] Because such waveguides are commonly prepared by a thermal diffusion process of metal ions or protons, thermally induced deterioration of the substrate has been investigated to improve the fabrication processes and the device characteristics. The introduction of moisture into the annealing atmosphere, for instance, has been effective in reducing the outward diffusion of lithium and in decreasing the generation of microdomains.[2,3] Nozawa and Miyazawa[4] recently reported that the growth of microdomains, caused by inward diffusion of titanium, could be significantly suppressed by introducing the proper amount of moisture and by using argon instead of oxygen gas (O$_2$). On the other hand, Koide *et al.*[5] reported that the thermal degradation of LN, caused by dry atmosphere annealing, also could be prevented by using a substrate whose hydroxide (OH) content was previously reduced, judging from an absence of the refractive-index anomaly at the annealed surface. These results indicate the importance of OH control in the system, i.e., both in LN and in the atmosphere, for the fabrication of high-performance LN devices.

From the standpoint of process simplicity, the dry atmosphere annealing seems to be practical, in that it avoids many operating parameters to adjust the moisture content in carrier gases. Furthermore, we previously have found a significant suppression of the dc drift phenomenon for optical modulator devices that were fabricated from a dehydrated LN substrate.[6,7] In this regard, it is necessary to investigate the influence of a dry atmosphere annealing on the surface morphology of the LN substrate, which consequently affects the device characteristics, such as optical insertion loss, bonding strength of coating layers, etc. Here, changes in the surface morphology of two different LN(000$\bar{1}$) substrates that contain low and high amounts of OH ions and are attributed to dry annealing have been systematically investigated using atomic force microscopy (AFM) within the temperature range of 400°—1000°C. The results reveal a surface roughening in the LN with greater OH contents within the lower temperature range, where an outward diffusion of OH from the substrate occurs, supporting the results by Koide *et al.*[5] Furthermore, at higher annealing temperatures, the growth of well-regulated steps is observed for both of the LN substrates. The step height has been measured to be a factor of $n/6$ (where n is an integer) of the c-axial length of LN.

II. Experimental Procedure

Two different LN substrates, 0.5 mm thick with mechano-chemically polished (0001) faces, were cut into 10 mm × 15 mm plates. Fourier transform infrared spectroscopy (FTIR) revealed that the one substrate contained 4.2×10^{19} cm^{-3} OH ions (hereafter called "HOH") whereas the other had 4.6×10^{18} cm^{-3} OH ions (hereafter called "LOH"). The LOH substrate was supplied by Nihon Kessho Koogaku Co. (Tatebatashi, Gunma, Japan) and had been thermally dehydrated before the polishing process.[5] The HOH and LOH samples were enclosed in a platinum box and annealed in a tube-type furnace at 150°C for 5 h and further at temperatures in the range of 400°—1000°C for 10 h, whereas dry O$_2$ with a dew point of less than -70°C was introduced into the furnace at a flow rate of 500 cm^3/min. The time that was required to heat the furnace from 150°C to the higher annealing temperature was fixed to be 2 h, and the cooling time to room temperature was ~ 5h.

The annealed samples were evaluated for the OH content using an FTIR spectrometer, and the surface morphology was evaluated by AFM. For each sample, the OH content, c, was calculated from the IR absorption constant, k, at ~3485cm^{-1} for OH stretch modes, using the formula $c = 3 \times 10^{19}k$ (in units of cm^{-3})[8]. The AFM observation was conducted in an air atmosphere using a Si$_3$N$_4$ cantilever in a noncontact mode (force reference of -0.087 nN) without any bias. Because the LN substrate was pyroelectrically charged, to prevent charging during the AFM observation, the sample was cut into pieces that were ~2 mm × 10 mm in size and fixed on the stage by a silver paste. Furthermore, the sample surface was hemmed in by silver paste, leaving a window for observation that was 1 mm × 1 mm in size.

III. Results and Discussion

Figure 1 shows the OH contents of HOH (indicated by open circles) and LOH (indicated by filled circles) before and after the annealing, both of which were measured by the FTIR method. The broken line in the figure denotes the detection limit of the measurements, i.e., the background level of the absorption profile. As is shown in the figure, the dehydration of the LN substrate occurred at a temperature of >500°C and finally stabilized near the detection limit. In the HOH samples, the remaining OH ions decreased to 1/20 of the initial contents.

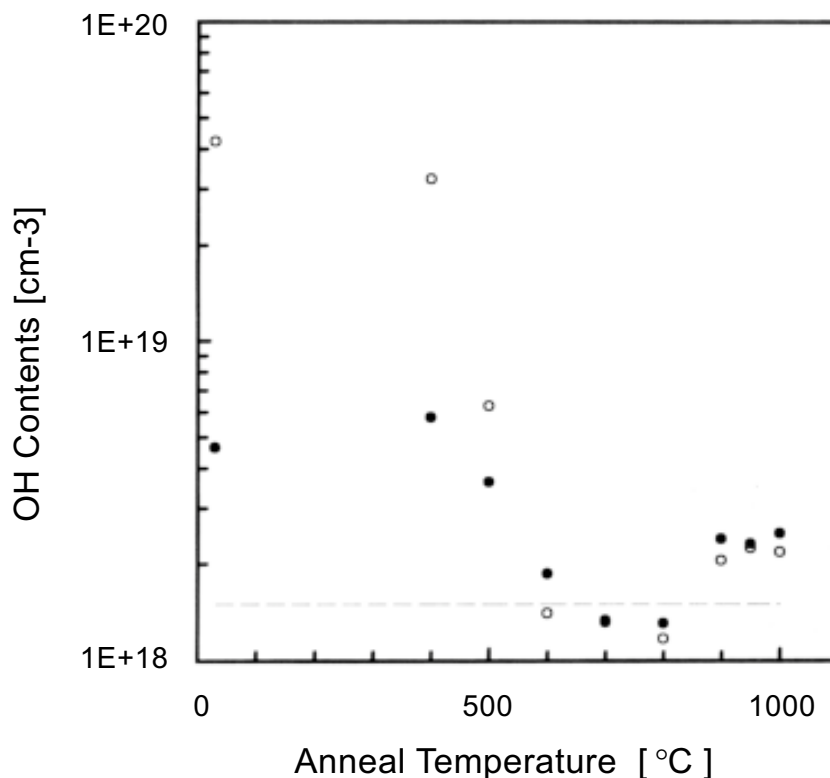Figure 2 exhibits the AFM image of the HOH sample surface

Fig. 1. OH contents of (○) conventional HOH and (●) dehydrated LOH LN substrates before and after the dry O_2 annealing at various temperatures.

before annealing, in which an area 2 μm × 2 μm in size was observed. The vertical axis, in nanometers, corresponds to the *c*-axis (<0001> direction) of the LN crystal. The horizontal axis (nearest the bottom edge of the micrograph), in micrometers, was almost parallel to the *a*-axis (<2110> direction). The peak-to-peak roughness of such a mechanochemically polished surface was measured as 1.7 nm for an area that is 2 μm × 2 μm in size and 2.5 nm for an area that is 10 μm × 10 μm in size. The unannealed LOH sample showed a similar surface morphology. The AFM images of surfaces after annealing for 10 h are shown in Figs. 3 and 4 for the HOH and LOH samples, respctively; the observed area size and direction were the same as those in Fig. 2. The images for the HOH samples annealed at 600°, 700°, and 800°C in Fig. 3, were plotted with a vertical-axis maximum of 30 nm, because of their significantly increased roughness, whereas the other images were displayed with vertical axis maxima of 10 nm. As shown for both samples, at annealing temperatures of <500°C, the initial morphology of the polished surface was maintained without any surface roughening.

In regard to the HOH sample, the surface morphology at 600°C deteriorated, as shown in Fig. 5 for the typical surface profile along a distance of 5 μm. The peak-to-peak roughness of this sample was 12 nm for its area of 2 μm × 2 μm. These were many precipitates that had diameters of 20–50 nm distributed over this surface. As the annealing temperature increased, the shape of the precipitates changed to a spindlelike shape that was ~50 nm × 120 nm in size at 700°C and ~120 nm × 300 nm in size at 800°C. Furthermore, they were distributed on the surface in a three-fold symmetry pattern, as shown in Fig. 6, which is a top view of the HOH sample that was annealed at 800°C (area of 2 μm × 2 μm). Here, the origin of the precipitates was speculated to be as follows, although crystallographic analysis of the surface was not performed at this moment. As is generally known, at temperatures of <900°C, a transformation between $LiNbO_3$ and $LiNb_3O_8$ occurs reversibly in a closed $LiNbO_3$ system.[3] In this regard, McCoy *et al.*[9] recently reported their transmission electron microscopy (TEM) investiga-

tion on the epitaxial growth of $LiNb_3O_8$ precipitates with three variant orientations on the LN(0001) surface that has been annealed at 750°C. The three-fold symmetry pattern observed in Fig. 6 was consistent with their result, leading to the possibility of $LiNb_3O_8$ growth on the dry-annealed HOH surface. Many surface voids that were similarly observed in Fig. 6 were supported to be caused by an islandlike growth of $LiNb_3O_8$ crystallites on the $LiNbO_3$ surface.

On the other hand, such surface roughening has never been found for the LOH samples, as shown in Fig. 4. The result suggests that the surface roughening, possibly due to $LiNb_3O_8$ growth, was induced by the large dehydration in the HOH substrate. It has been previously reported that, in the predehydrated LN substrates, i.e., the LOH substrate, an evaporation of lithium from the substrate was effectively suppressed, even for the dry O_2 annealing at higher temperatures (~1000°C), whereas much lithium evaporated from the similarly annealed conventional substrate, i.e., HOH.[2,5,10] Therefore, even at lower temperatures, there is a possibility that the removal of OH ions from the LN crystal enhances the diffusion of lithium ions through the LN
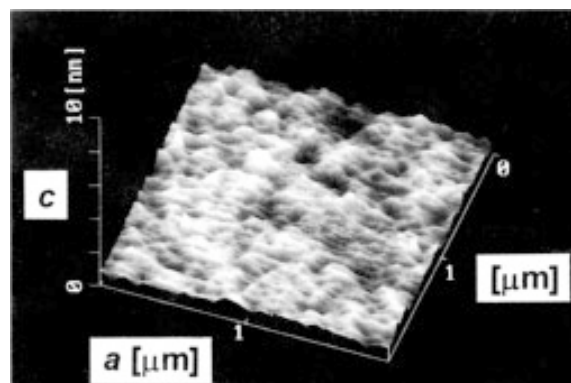

Fig. 2. AFM image of the as-received HOH LN(000$\bar{1}$) substrate surface before annealing; the observed area size was 2 μm × 2 μm. Maximum of the vertical axis was 10 nm.
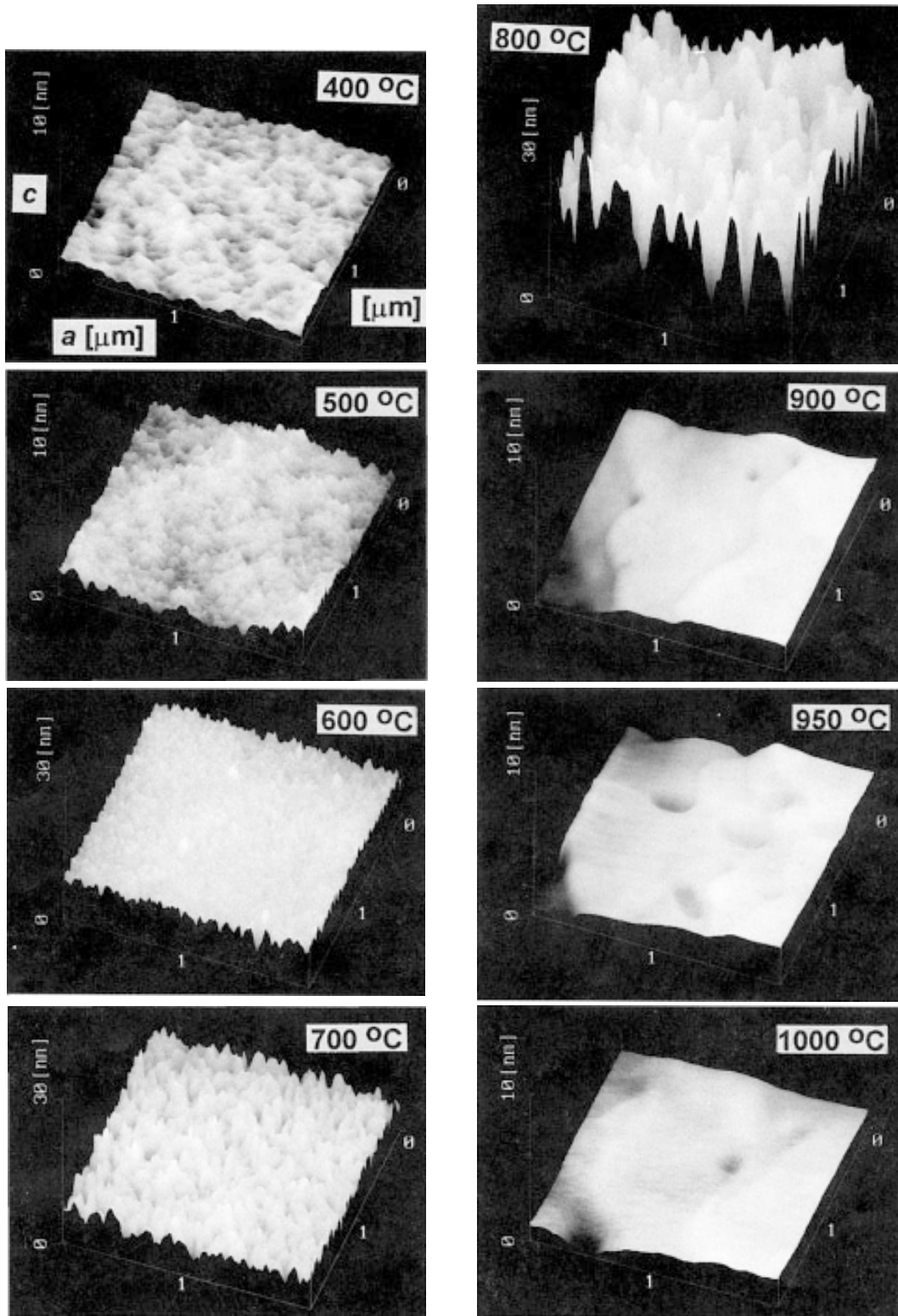
Fig. 3. AFM image of conventional HOH LN(000$\bar{1}$) substrates dry annealed at 400°—1000°C; the observed area sizes were 2 μm × 2 μm. Maximum of the vertical axes was 10 nm, except for the images of 600°, 700°, and 800°C (for which the maximum was 30 nm).

crystal and leads to a transformation from $LiNbO_3$ to $LiNb_3O_8$ at the surface.

In contrast, when the annealing temperature of the HOH sample was increased further, to a temperature of >900°C, the precipitates vanished completely and the steplike surface appeared. Such a stepped surface in the HOH samples was similar to that which was observed for the LOH samples (see Fig. 4), except for the existence of many pits with flat bottoms on the former (see Fig. 3).

In the LOH samples, however, the surface morphology changed simply as the temperature increased. At 700°C, many equivalent triangle-shaped plates appeared, with sides that were ~200 nm long and almost parallel to the *a*-axis of LN. Such triangle-shaped plates aggregated and formed a terrace ~1 μm wide, suggesting an infant stage of the surface step formation. As the temperature increased, the triangle plates seemed to evolve with fewer exposed edges and formed the flat terraces at 900°C. On these steplike surfaces, the step edges were not
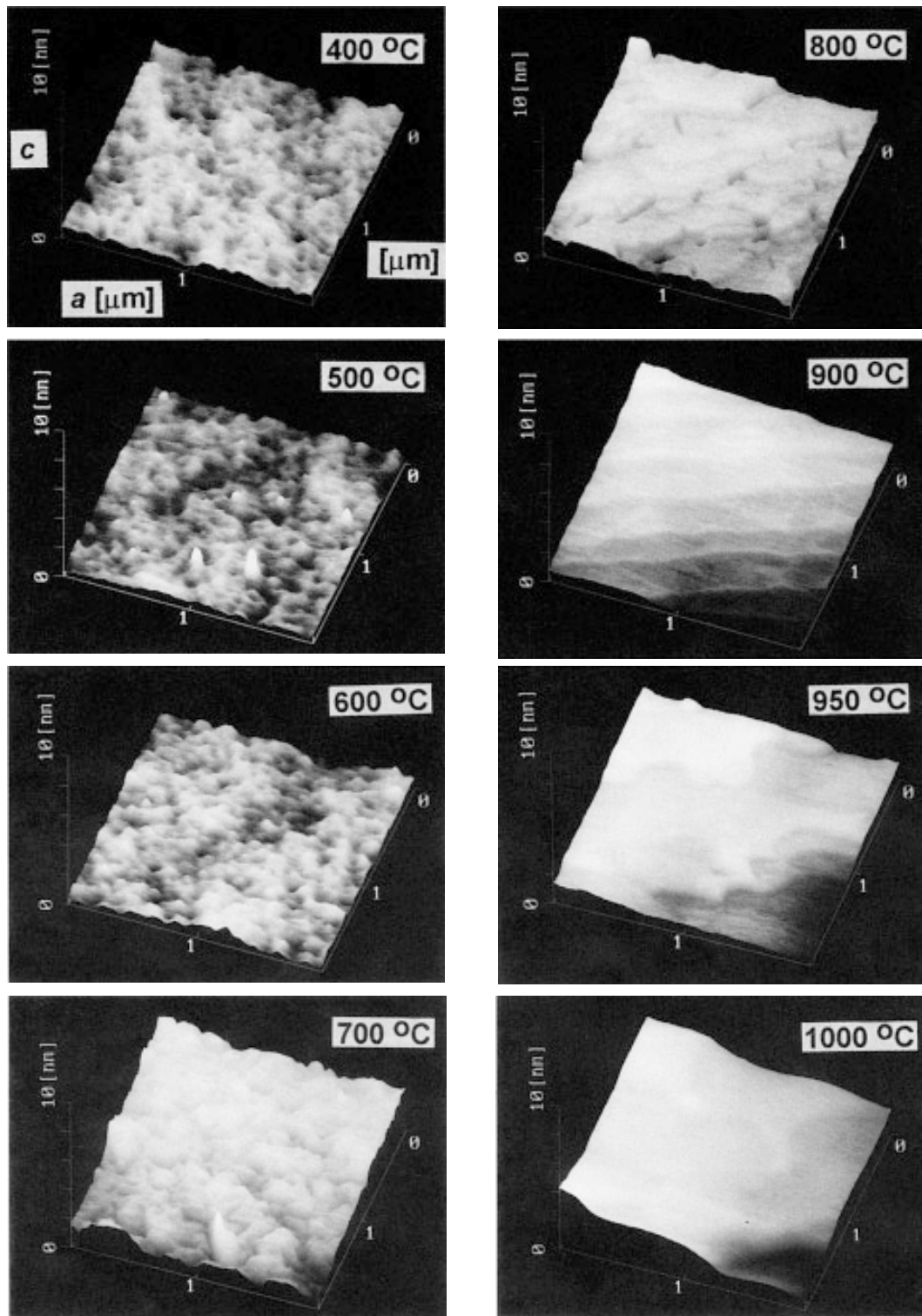
Fig. 4. AFM image of dehydrated LOH LN(000$\bar{1}$) substrates dry annealed at 400°-1000°C; the observed area sizes were 2 μm × 2 μm. Maximum of the vertical axes was 10 nm.

parallel to the LN *a*-axis. Although the crystallographic direction was not defined accurately in the present AFM observation, the angle between the *a*-axis (<2110> direction) and the step edge was measured to be ~ 25°. The terraces grew larger, accompanied by a curving of the step-edge lines, as the annealing temperatures increased further.

Figures 7(A)—(C) show typical cross sections of the step surface of LOH samples annealed at 800°, 900°, and 950°C, respectively. The minimum step height, *h*, was measured to be ~ 0.23 nm, and the other step heights were integer multiples of *h*, i.e., *2h*, *3h*,...; numerous mea-

surements for similar samples derived *h* to be 0.25 ± 0.03 nm (0.03 was the standard deviation). This distance corresponds to 1/6 of the *c*-axis length of LN crystal (1.38 nm × 1/6 = 0.23 nm) — in other words, the minimum distance between (O — O) planes of the layered LN crystal structure. These results indicate that, at temperatures of >800°C, the crystalline LiNbO$_3$ phase dominated the surface almost completely, as excepted from a phase diagram for the Li$_2$O-Nb$_2$O$_5$ system.[3]

A similar stepped surface with step heights of *n* × 0.25 nm (*n* is an integer) also was obtained for the HOH surface after annealing at temperatures of ≥900°C, although the surface had been covered
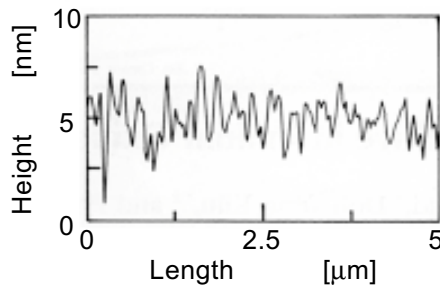
Fig. 5. AFM surface profile of the HOH LN substrate dry annealed at 600°C.

by precipitates and significantly roughened at lower temperatures. In regard to the disappearance of the surface precipitates ($LiNb_3O_8$ possibly), we assumed that at least some of the precipitates were absorbed into the substrate surface via a retransformation to the $LiNbO_3$ phase in the closed system. Such retransformation of the precipitates to the $LiNbO_3$ seems to be a reason for the irregularly shaped terraces with greater step heights that are observed in the HOH surface (see Fig. 3). A crystallographic analysis using a surface-sensitive method is necessary to investigate the phenomenon further.

IV. Conclusion

The surface morphology of the $LiNbO_3(0001̄)$ (LN) substrates was investigated using atomic force microscopy, from the standpoint of thermally induced changes due to dry O_2 annealing. The change depended largely on the amounts of OH ions remaining in the virgin substrates. At the temperatures for increased removal of the OH from the substrate, the surface was significantly roughened by the growth of precipitates. In the dehydrated LN substrate, however, such surface roughening did not occur. At higher annealing temperatures, the surface changed to a steplike morphology, independent of the OH contents, with the height corresponding to $n/6$ of the LN c-axis length (n is an integer). These results suggest that the dehydrated LN substrates were amenable to a dry atmosphere heat treatment without any surface roughening. Furthermore, the
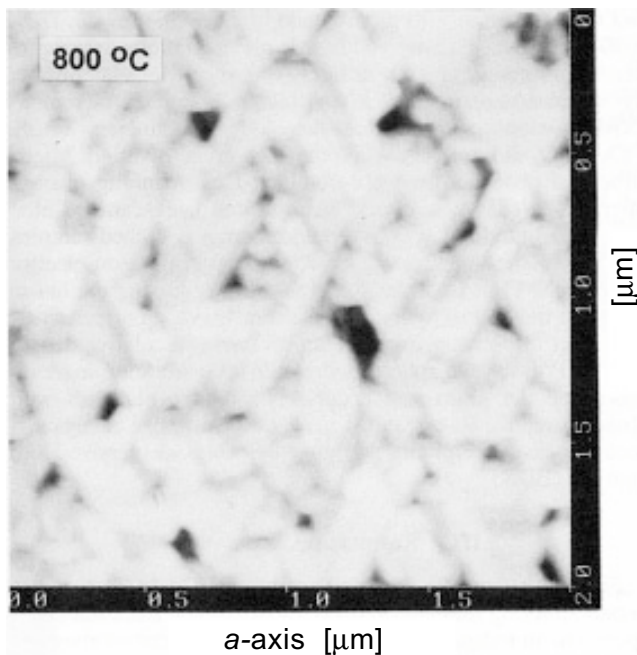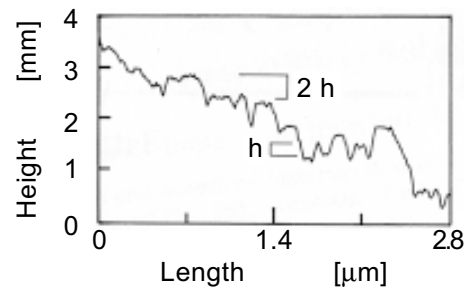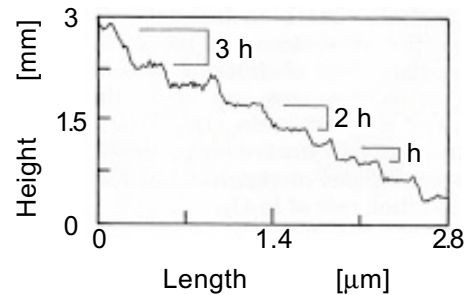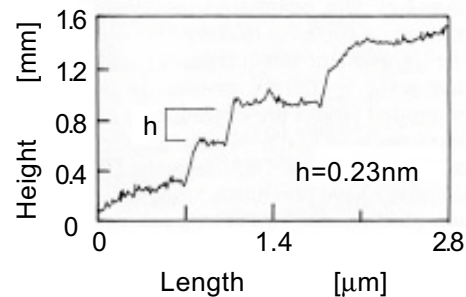

Fig. 6. AFM top-view image of the HOH LN substrate dry annealed at 800°C; the area size was 2 μm × 2 μm, and the horizontal axis was the a-axis (<2110> direction) of the LN(0001).

(A)

(B)

(C)

Fig. 7. AFM surface profiles of the dehydrated LOH LN substrates dry annealed at (A) 800º, (B) 900º, and (C) 950ºC; the value of h was measured to be ~0.23 nm.

high-temperature annealing (800º—900ºC) was a suitable process for removing a surface layer that was possibly deteriorated by the polishing process and could achieve a flat surface.

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