Surface precipitates on single crystal LiNbO3 after dry-etching by CHF3 plasma

Kaori Shima
Advanced Materials Research Division, New Technology Research Laboratories, Sumitomo Osaka Cement
Co., Ltd., 585 Toyotomi-cho, Funabashi-shi, Chiba 274, Japan

Naoki Mitsugi and Hirotoshi Nagata
Optoelectronics Research Division, New Technology Research Laboratories, Sumitomo Osaka Cement
Co., Ltd., 585 Toyotomi-cho, Funabashi-shi, Chiba 274, Japan

(Received 19 February 1997; accepted 5 August 1997)

The CHF3 electron cyclotron resonance (ECR) plasma etched LiNbO3 (LN) surface was analyzed chemically and crystallographically to investigate the dry-etch machining process for LN crystal, which was recently needed to obtain broader-band optical modulators. The etched surface was entirely covered with amorphous-like precipitates having Å‘70 nm diameter. These precipitates (or a part of them) were thought to be LiF from Auger electron and x-ray photoelectron spectroscopy. The results indicated that the LiF was formed and remained on the etched surface while the Nb was almost completely removed.

In order to expand the optical bandwidth of $LiNbO_3$ (LN) based modulators, the plasma dry-etching technique is applied to fabricate a trench structure on the LN substrate surface, in which the LN is removed to a depth of about 3É m along the optical waveguide.[1,2] Such a structure effectively reduces the permittivity of the substrate, broadening the bandwidth while reducing the driving voltage. Dry-etching of the LN is performed fluorocarbons such as CF_4 and CHF_3 rather than Ar, in order to prevent surface damage by high energy ions.[1,2] Jackel et al. reported originally the reactive ion etching of the LN and suggested the possibility of the formation of a thermally stable compound of Li with halogen during the chemical etching process.[3] They recommended mixing Ar into the chemical etching gases to physically remove the Li-halides. However, to our knowledge, there has been no report to show any evidence for the existence of the Li-halide layer due to the dry-etching. Here, we investigated the LN surface etched by an electron cyclotron resonance (ECR) plasma of CHF_3 and confirmed the formation of LiF on the surface. The CHF_3 was chosen in this experiment because the coexistence of F and H was commonly known to be suitable for the etching of oxide materials.[4]

Commercial X-cut (crystallographic a-face) and Z-cut (c-face) LN substrates with an optically fiat surface were treated by an ANELVA L-310R ECR plasma etcher. After the substrate was inserted, the etching chamber was evacuated to about 3Å~10^{-5} Pa by a cryopump. Then, CHF_3 was introduced into the chamber at a rate of 3 sccm, and the pressure was kept at about 0.01 Pa. Microwave power and high voltages applied to the magnet and bias electrode were chosen to generate a stable CHF_3 plasma and to obtain a higher etching rate. The substrate holder, made of a sintered SiC, was cooled by water during the etching. The typical etching rate in this experiment was 500 to 600 nm/h for both the X-cut and the Z-cut LN substrates.

The etched LN surface became hazy. Figures 1 (a) and 1(b) show atomic force microscopic (AFM) images of the substrate surfaces before and after the CHF_3 ECR plasma etching for 4 h, respectively. The image in Fig. 1(a) was a typical morphology for a mechanochemically polished LN surface.[5-7] However, due to the CHF_3 plasma etching, the surface was covered entirely with Å‘70nm diameter precipitates. The peak-to-peak surface roughness in the observed 2É mÅ~2É m area was 2.2nm for Fig. 1(a) before the etching and 43nm for 1(b) after the etching. On the other surface etched for 2 h, similar precipitates were observed, including many smaller particles. On such a surface, x-ray microanalysis was used to detect a small amount of F in addition to Nb and O.

In order to confirm the existence of F on the surface, Auger electron spectroscopy was carried out for the 1-h-CHF_3 plasma etched sample accompanied with Ar ion etching. The Ar ion etching rate for this LN sample was calculated to be 8 nm/min from the depth of the Ar ion etched crater measured by a stylus method. To prevent a charge-up of the sample, the acceleration energy, current, and size of the incident electron beam had been set at 3kV, 1Å~10^{-8} A, and 10É m, respectively. In the measurement, the windows for the energy detector were fixed at Li KLL, Nb MNN, C KLL, O KLL, and F KLL peaks which were clearly detected from the surface before the Ar ion etching. It was noted

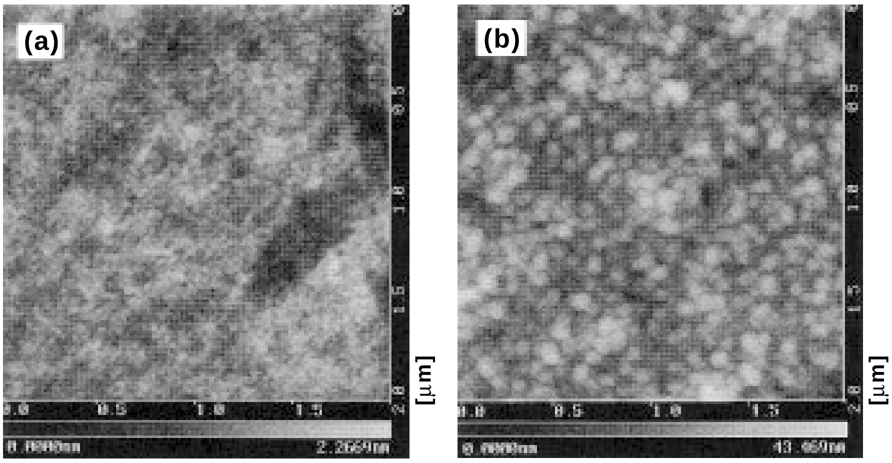

FIG. 1. AFM images for the LiNbO$_3$ substrate surface (a) and the CHF$_3$ plasma etched LiNbO$_3$ substrate surface (b). The 2µm × 2µm area was observed for both samples.

that, for the virgin LN surface without CHF$_3$ plasma etching, the F KLL peak was not observed. Figure 2 shows a change of the Auger electron peak intensities measured after Ar ion etching treatments. The horizontal axis of Fig. 2 denotes the cycle number of the Ar ion etching (each 4 s) and the measurement, corresponding to the depth from the surface. The intensity of the F *KLL* peak decreased rapidly after several Ar ion etching cycles, and then damped gradually within 70-80 etch cycles, which corresponded to about 50 nm depth from the surface. The C *KLL* peak was confirmed to disappear beyond about 100nm depth, which is not shown in the figure. These data suggested that the LN surface was fluoridated during the CHF$_3$ plasma etching treatments.

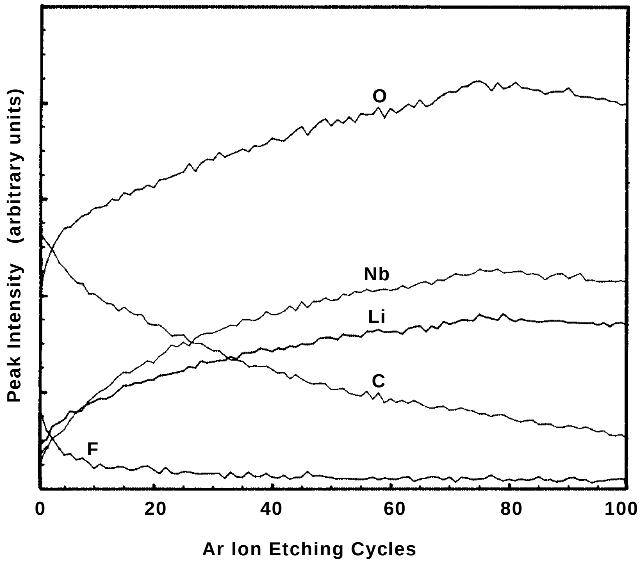

FIG. 2. Distribution of Li, C, F, O, and Nb along the depth direction for the CHF$_3$ plasma etched LiNbO$_3$ measured by an Auger electron spectroscopy. The full horizontal axial length corresponds to about 70 nm depth from the surface.

Next, to investigate the chemical state of the F, a similar sample was analyzed by an x-ray photoelectron spectrometer (XPS) using a Mg Kα incident x-ray beam with about a 1mm diameter. The angles between the sample surface and analyzer and between the surface and the source were 45 and 90°, respectively. Ar ion etching was not performed in this measurement to prevent a reduction of the surface due to the interaction with high energy ions in the high vacuum atmosphere. Figure 3 reveals the peak profiles obtained for F 1s, O 1s, C 1s, Nb 3d, and Li 1s photoelectrons. The binding energy in the horizontal axes was calibrated by the C 1s peak for C-C and/or C-H configuration at 284.8 eV. As is seen, the main peak for F 1s appeared near 685 eV with the small shoulder peak at about 688 eV. The binding energy of this main peak corresponded to that for the F bonded with a metal (685-686 eV for LiF), while the shoulder peak was attributed to C-F bonding.[8] The O 1s peaks could be identified as a peak from oxidized metals around 530 eV (e.g., $\sim$531 eV for Li$_2$O and $\sim$530.3 eV for LiNbO$_3$), C=O bonding at about 532 eV, and C-O-C bonding at about 533 eV.[8] The observed C 1s peaks could be attributed to C-C bonding at 284.8 eV, C-O and/or C*-CF$_x$ at 285.5-286.5 eV, C=0 and/or -CF at 287-288 eV, and O=C-O at 289 eV.[8] The Nb 3d$_{5/2}$ peak observed at 207 eV seemed to come from oxidized Nb such as LiNbO$_3$ ($\sim$207.1 eV) and Nb$_2$O$_5$ (206-208 eV).[8] Although the Li 1s peak was very weak, its binding energy, about 56 eV, corresponded evidently to that for LiF at 55.7-56.7 eV rather than for LiNbO$_3$ at about 54.8 eV.[8] The additional peak at 60 eV which appeared near Li 1s was due to Nb 4s for LiNbO$_3$. As a result, the Li on the etched surface was almost completely combined with F, while the Nb existed as LiNbO$_3$. Further, the C due to the etching gas also remained on the surface, in addition to the carbons combined with oxygen which were the main part of

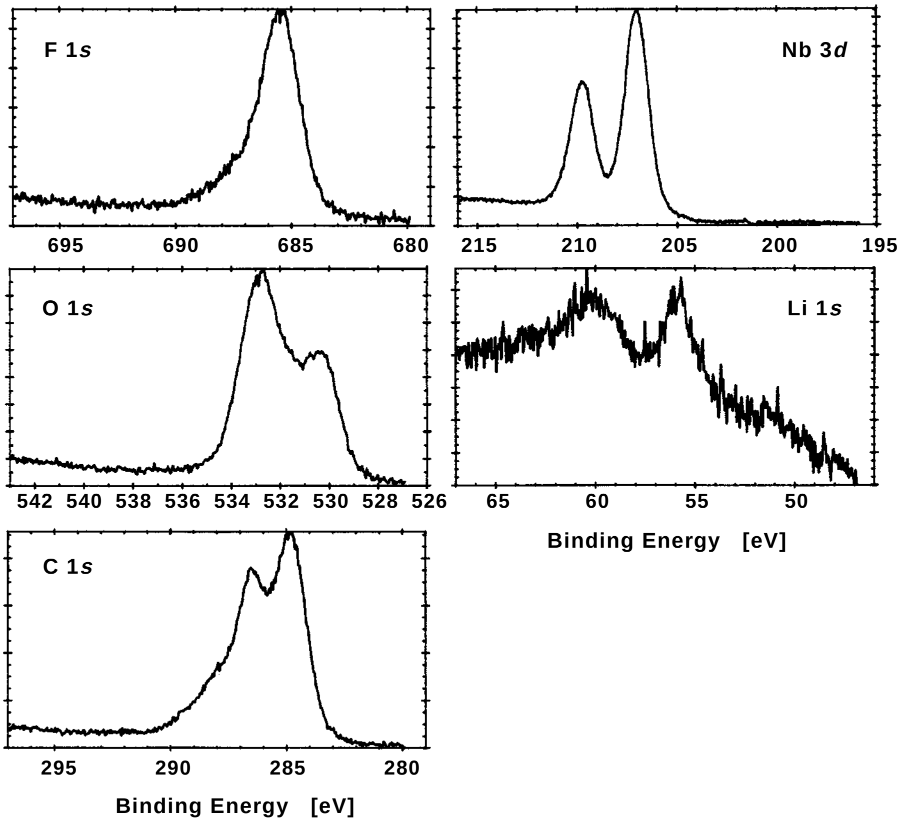

FIG. 3. X-ray photoelectron spectroscopic results for the CHF_3 plasma etched $LiNbO_3$. No surface cleaning by Ar ion etching was carried out before the measurement.

the observed C 1s peak and considered to come from surface contaminants. The atomic percents for F, O, C, Nb, and Li were estimated to be 8, 34, 48, 4, and 6%, respectively.

Finally, the structure of the surface precipitates on the CHF_3 plasma etched LN of Fig. 1(b) was investigated by a glancing angled x-ray (XRD) and a transmission electron (TEM) diffractometer. In both measurements, no diffraction peak specific to the precipitates was detected. It is important to note, the TEM observation was performed only for the precipitate layers after a conventional ion-thinning of the sample from the backside and a halo pattern without any diffraction spots was obtained, suggesting the precipitates were amorphous-like.

The above-mentioned results suggested the formation of Li fluoride, LiF, during the CHF_3 plasma etching of the $LiNbO_3$ surface. It is likely that this LiF is amorphous rather than crystalline. On the other hand, the Nb existed as an oxide, possibly $LiNbO_3$, on the etched surface, indicating the Nb was successfully volatilized by the CHF_3 plasma etching. In the dry-etching process for the $LiNbO_3$ using fluorocarbons, the removal of the LiF precipitates is a key issue for getting a high etching rate and a smooth surface without a chemically deteriorated layer.

ACKNOWLEDGMENTS

The authors gratefully thank Mr. Takano of Foundation for Promotion of Materials Science and Technology of Japan for XPS analyses and Dr. Min of Sumitomo Osaka Cement for the helpful discussion.

REFERENCES

1. M. Minakata, Electron. Commun. Jpn. Part 2 **77**, 37 (1994).
2. K. Noguchi, O. Mitomi, H. Miyazawa, and S. Seki, J. Lightwave Technol. **13**, 1164 (1995).
3. J. L. Jackel, R. E. Howard, E. L. Hu, and S. P. Lyman, Appl. Phys. Lett. **38**, 907 (1981).
4. Handbook of Plasma Materials Science, edited by K. Akashi (Ohmsha, Tokyo, 1992).
5. H. Nagata and K. Shima, Jpn. J. Appl. Phys. **35**, 4040 (1996).
6. H. Nagata, T. Sakamoto, H. Honda, J. Ichikawa, E. M. Haga, K. Shima, and N. Haga, J. Mater. Res. **11**, 2085 (1996).
7. H. Nagata, K. Shima, and J. Ichikawa, J. Am. Ceram. Soc. **80**, 1203 (1997).
8. Handbook of Photoelectron Spectroscopy, edited by J. Chastain (Perkin-Elmer Co., Eden Prairie, MN, 1992).