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ABSTRACT

Ion-cutting of piezoelectric LiNbO$_3$ (LN) thin film provides a material platform for the design and fabrication of novel integrated photonics and RF MEMS devices. In this paper, the ion-slicing mechanisms of He-implanted LN with different orientations are investigated. The anisotropy of film exfoliation is observed on LN wafers with different orientations. The Z-cut LN shows regular surface blistering and “plate-like” exfoliation, while the Y-cut LN shows the unique “rolled-up” exfoliation. Two types of defect, i.e. the pressure-related plateau defect and the stress-related crack defect, are observed to contribute to the film exfoliation. Moreover, the defect evolution in H-implanted LN is investigated. In comparison with the He-implanted LN, implanted H ions are mainly trapped by O-H bond and the implantation-induced strain is not strong enough, which are inadequate to form the continuous crack. Therefore the H ions are not favorable for the mass production of LNOI substrates.

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I. INTRODUCTION

As one of the well-known ferroelectric materials, lithium niobate (LN) has attracted great attentions for the applications of electro-optical modulators, surface acoustic wave resonators and holographic storage elements due to its high Curie temperature, excellent optical transparency, high electro-optic coefficients and large piezoelectric coefficients.$^1$ In comparison with the bulk LN wafers, the LN thin films effectively reduce the device diameters, operating voltages and temperature drift.$^{2–5}$ Hetero-epitaxy methods such as molecular beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD) have been widely used for the growth of the LN films in the past decades.$^6$ However, the film quality is dramatically deteriorated due to the mismatch of the crystal structure and lattice between the LN film and the substrate. In recent years, single-crystalline LN films have been fabricated using the ion-cutting technique, and the LN-on-Insulator (LNOI) substrates provide a material platform for various novel integrated photonic devices and piezo MEMS.$^7–9$

The ion-cutting technique combines crystal ion slicing and wafer bonding. The ion slicing of LN is crucial for fabricating the LNOI substrate, and a deep understanding of the slicing mechanism is beneficial to improve the film quality. LN is highly anisotropic, while the photonic and acoustic devices are fabricated on LN with different orientations. LNOI substrates with various orientations are required depending on the applications. More recently, Y-cut LNOI has been applied in RF MEMS with high figure of merit (FOM), photonic integrated circuits and acoustic-optical devices due to the high electromechanical coupling coefficient ($k_t^2$) and low optical
loss. However, the ion-slicing mechanism was mainly investigated on the Z-cut LN, while the slicing mechanism of the Y-cut LN was seldom investigated. In addition, the ion slicing of LN was mainly reported by using He ion implantation, which is very different from the slicing of semiconductors such as Si, SiC and GaN. Since H ion has a small atomic mass which introduces low residual damage in the transferred films and the H ion implantation is more efficient than He ion implantation due to the high flux generated by the implanter, ion slicing by using H ion implantation is preferable for the mass-production of LNOI. It is interesting to compare the defect formation mechanism in He implanted and H implanted LN and to investigate the H evolution in LN.

In this study, we investigated the ion slicing of Y-cut LN in comparison with that of the Z-cut LN. LN with different orientations presented disparate exfoliation behaviors, and the exfoliation activation energies were calculated. In addition, the defect formation in H-implanted LN as well as He-implanted LN was investigated, and the defect evolution mechanisms were compared.

II. EXPERIMENTAL DETAILS

Single-side polished Z-cut and Y-cut LN wafers were implanted by 115 keV He ions at room temperature with a fluence in the range of \( (2 \sim 5) \times 10^{16} \text{ cm}^{-2} \). During the implantation, the wafers were tilted 7° from normal to minimize the channeling effect. The He ion implantation led to the formation of the defects located near 480 nm underneath the surface. After He ion implantation, the LN wafers were annealed in the N\(_2\) atmosphere at the temperature ranging from 200 °C to 300 °C. Then, the optically detectable surface morphology change was inspected using optical microscopy (OM), and the defect evolution in LN was observed by cross-sectional scanning electron microscopy (SEM). Moreover, the Y-cut LN implanted by 75 keV H ions with the fluence of \( 1.2 \times 10^{17} \text{ cm}^{-2} \) was prepared. The defect evolution of H-implanted and He-implanted LN was compared. The implantation-related displacements and lattice distortion in the samples were characterized using the Rutherford backscattering/channealing (RBS/C) and the cross-sectional transmission electron microscopy (XTEM). OH-transmission spectra were acquired using Fourier transform infrared spectroscopy (FTIR) to analyze H-related substitution. The implantation-induced strain was assessed by high-resolution X-ray diffraction (HRXRD).

III. RESULTS AND DISCUSSION

Z-cut and Y-cut LN exhibit totally different surface exfoliation behaviors as shown in Fig. 1. Fig. 1a shows the OM image of the Z-cut LN implanted with \( 2.5 \times 10^{16} \text{ cm}^{-2} \) He ions after annealing at 300 °C for 20 minutes. Plenty of blisters appear on the sample surface. The surface blisters distribute uniformly and dispersedly, and the size of blisters varies from 3 \( \mu \text{m} \) and 10 \( \mu \text{m} \). When the He fluence is increased to \( 5 \times 10^{16} \text{ cm}^{-2} \), “plate-like” exfoliation is observed as shown in Fig. 1b. Large areas of LN films are exfoliated while some unexfoliated island regions remain on the surface as marked in

![FIG. 1. Surface morphology of Z-cut and Y-cut LN after He implantation and annealing. The Z-cut LN shows surface blistering and “plate-like” exfoliation (a)-(b), and the activation energy is calculated to be 1.29 eV (c). The Y-cut LN shows the “rolled-up” exfoliation (d) and the “rolled-up” process is recorded (e). The activation energy of Y-cut LN is calculated to be only 0.54 eV (f).](image-url)
Fig. 1b. The shape of the exfoliation region is formed by the distribution of the He-induced stress-related cracks. The surface blistering and “plate-like” exfoliation of Z-cut LN are similar to the exfoliation behavior of semiconductors such as Si, SiC and InP. The annealing time required to form optically detectable blisters was defined as the exfoliation time. For the Z-cut LN implanted with \( 2.5 \times 10^{16} \text{cm}^{-2} \) He ions, the Arrhenius plot of the exfoliation time and the reciprocal of the temperature \( T \) is plotted in Fig. 1c, and the activation energy is calculated to be 1.29 eV. Fig. 1d shows the OM image of the Y-cut LN implanted with \( 2 \times 10^{16} \text{cm}^{-2} \) He ions after annealing at 230 °C for 20 minutes. Parts of the sample surface are exfoliated and the exfoliated films roll up due to the implantation-induced strain. However, the surface morphology of the unexfoliated region is similar to that of the pristine LN. The dispersive and uniform surface blisters appearing on Z-cut LN are not observed on the Y-cut LN. When the He fluence is increased to \( 3 \times 10^{16} \text{cm}^{-2} \), massive linear defects are observed on the surface as shown in Fig. 1e. These linear defects assemble themselves in a parallel row aligned along the x-direction. The distribution of the linear defects is related to the activation energy to form the exfoliation process of Y-cut LN. With annealing, the surface was exfoliated and the exfoliated films rolled up along the z-axis and extend along the x-axis. The animated image is shown in the video supplementary material.

For the Y-cut LN implanted with \( 2 \times 10^{16} \text{cm}^{-2} \) He ions, the exfoliation time at different annealing temperature was recorded. The Arrhenius plot is shown in Fig. 1f, and the activation energy is calculated to be 0.54 eV. The activation energy for exfoliating Y-cut LN of 0.54 eV is much smaller than that for exfoliating Z-cut LN of 1.29 eV.

As the exfoliation behavior of the Y-cut LN was quite different from the exfoliation of most materials, the defect evolution in the Y-cut LN implanted with \( 2 \times 10^{16} \text{cm}^{-2} \) He ions was investigated in details. Fig. 2a shows the cross-sectional SEM image of the sample after annealing at 190 °C. The micro-crack defects locate at the depth of about 485 nm and two types of defect can be figured out, i.e. the Type-I defect and the Type-II defect as marked in Fig. 2a. It is well known that He implantation induces large amounts of nano-defects and these defects migrate, accumulate, and grow up to microcracks during annealing. The role of He is to generate pressure inside the microcracks and to increase the stress around the microcracks. The cracks grow laterally when the stress intensity factor at the crack tip exceeds the fracture of LN, and form the Type-I defect which is parallel to the sample surface. In addition, LN is a highly-brittle material and the stress in the material generates plastic deformation and crystal cracks. As shown in the SEM image, the angle between the Type-II crack and sample surface is about 32°. The direction of the Type-II is consistent with the [102] lattice plane as indicated by the LN lattice structure shown in the inset of Fig. 2a. The Type-II defect is inferred to be the crystal crack caused by the implantation-induced stress. During the annealing, the Type-I and Type-II defects propagate, coalesce together, overlap and eventually form a continuous cleft crack between the exfoliated LN film and the substrate as the SEM image shown in Fig. 2b. The defect evolution is schematically shown in Fig. 2c. The He ions diffuse to fill in the cracks as the arrows marked and to increase the inner pressure to form the Type-I cracks. He implantation induces large stress and generates the stress-related Type-II cracks. The Type-II cracks serve as an intermediate to conjoin the Type-I cracks and accelerate the formation of the cleft crack. The angle between the Type-I crack and the Type-II crack is important for the crack propagation, and therefore impacts the exfoliation efficiency of LN with different orientation. The angle is about 32° in the Y-cut LN while it is about 58° in the Z-cut LN. Smaller angle means longer projected horizontal length, and it is more efficient for the Type-II crack to conjoin the adjacent Type-I cracks. Therefore, the exfoliation activation energy for the Y-cut LN is smaller than that for Z-cut LN. In addition, the cracks propagate laterally with the assistance of the Type-II crack easily, and the ratio of the delaminated height and the cleft length is small. Though the inflation cannot be inspected by the optical microscopy, a cleft crack might have been formed below the surface of the unexfoliated region in Fig. 1d.

It is well known that applying H ion implantation for ion-slicing is better than other ions due to the reduced damage induced...
by lighter H ion. However, almost all the reported LN films were sliced using the He ions instead of the lighter H ions. Implanting H ions in LN is a usual proton-exchange method to fabricate the LN waveguide, but the effect of H on the slicing of LN is seldom investigated. In our experiment, the optical transmittance of LN was significantly reduced after the H implantation due to the strong visible light absorption, but it was partially recovered after annealing at 300 °C for 20 minutes. However, no surface blistering or exfoliation was observed on the surface. The defect evolution of H-implanted LN was investigated.

The lattice damage induced by H implantation and the damage revolution after the annealing are analyzed using the Rutherford backscattering spectroscopy in channeling mode (RBS/C). RBS/C is sensitive to the atoms displaced from the crystalline position, and Nb-related part of the RBS/C spectra are plotted in Fig. 3a. For the H-implanted sample, a peak in backscattering yield at channel 530 comes from the direct scattering from the displaced atoms in LN crystal as indicated by the red line in Fig. 3a. However, the peak is flattened after the annealing process blue line in Fig. 3a, which suggests that the implantation-induced defects are recovered rather than forming the cracks for film exfoliation. Fig. 3b shows the XTEM image of the H-implanted LN after the annealing, no defect or crack is observed near the mean projected range $R_p$. Both the RBS/C and the TEM image indicate that the implantation-induced nano-defects cannot aggregate and grow up during the annealing.

The damage and ion distribution differences between the He ion implantation and the H ion implantation are analyzed. Fig. 4a plots the profiles of the ion concentration and the dpa (displacements per atom) acquired using the SRIM (Stopping Range in Matter) simulation. The XTEM image of the H-implanted LN after the annealing, no defect or crack is observed near the mean projected range $R_p$. Both the RBS/C and the TEM image indicate that the implantation-induced nano-defects cannot aggregate and grow up during the annealing.

FIG. 3. (a) RBS/C spectra of H-implanted LN before (As-impl.) and after annealing (Annealed). The random and aligned spectra of pristine LN crystal are also given for comparison. (b) The XTEM image of the H-implanted LN after annealing. No cracks are observed.

FIG. 4. (a) Ion concentration and dpa profile simulated by SRIM. (b) FTIR spectra of the H-implanted LN. (c) The XRD curves of H-implanted and He-implanted LN.
2 × 10¹⁶ cm⁻² as it is sufficient for the Y-cut LN exfoliation. Although the concentration of the H ions is about 5 times higher than that of the He ions, the dpa induced by the H implantation is only 80% of the dpa induced by the He implantation. Therefore, we can infer that the utilization ratio of the implanted H ions is low. Previous analysis suggests that the implanted ions increase the inner pressure of the defect and form the Type-I cracks, while the implantation-induced stress causes the crack of LN and form the Type-II cracks. The evolution of H ions and stress were investigated. The implanted H ions usually bond with the lattice atoms or vacancies. In LN, the H exists in a form of OH⁻ which can be measured using FTIR as shown in Fig. 4b. As the H may be introduced into LN during the CZ growth of LN crystals, the FTIR spectrum of the pristine sample is plotted as the reference. The OH⁻ mode at about 3484 cm⁻¹ in the pristine LN is very weak, suggesting that the H content is small in the pristine LN. After H implantation, the implanted H ions combined with the O atom in LN, and the transmittance at the OH⁻ mode decreased. However, the OH⁻ peak still exists after the annealing, which means that the H cannot be released from the O-H bond. Therefore, the H ions are trapped by the O-H bond and cannot diffuse into the nano-defects to increase the inner pressure effectively, which hinders the formation of Type-I crack. Fig. 4c shows the XRD curves of the H-implanted and He-implanted LN. Both the H implantation and the He implantation create out-of-plane tensile strain as indicated by the interference fringers extending from the left side of the (030) LN diffraction peak. The H-induced strain is evaluated to be only 0.6% (H As-impl.) while the He-induced strain is about 0.76% (He As-impl.). As the Type-II cracks are created in the strained LN, the small strain is detrimental for the crack formation in the H-implanted LN. Both the trapping of H ions in O-H bond and the weak stress in the H-implanted LN impede the generation of the micro-cracks efficiently and the formation of the continuous cleft crack. Therefore, H implantation is not feasible for the film exfoliation of LN.

IV. SUMMARY

In this study, the exfoliation mechanism of Y-cut LN was compared with the Z-cut LN implanted. The Z-cut LN shows surface blistering and “plate-like” exfoliation which is similar to semiconductors such as Si, but the Y-cut LN shows the unique “rolled-up” exfoliation. The exfoliation activation energy of Y-cut LN is 0.54 eV, which is much smaller than that of Z-cut LN as 1.29 eV. Two types of cracks, i.e. the pressure-induced plateau crack and the stress-induced crystal crack, were observed to grow up to a continuous cleft crack. In addition, the defect evolution of H-implanted LN was investigated in comparison with the He-implanted LN. The implanted H ions are trapped by the O-H bond and the implantation-induced strain is inadequate to facilitate the formation of both Type-I and Type-II cracks. Therefore, the He ions are the optimized ions for the mass-production of LNOI substrate using ion-cutting method.

SUPPLEMENTARY MATERIAL

See supplementary material for the recorded video of the rolled-up process of the sliced Y-cut LN film.

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