Surface modification of single crystal LiTaO$_3$ by H and He implantation

Changdong Ma$^{a,b}$, Fei Lu$^{b,*}$, Lei Jin$^c$, Bo Xu$^b$, Ranran Fan$^b$

$^a$Department of Radiation Oncology, Qilu Hospital, Shandong University, Jinan, Shandong 250012, China
$^b$School of Information Science and Engineering, Shandong University, Jinan, Shandong 250100, China
$^c$Ernst Ruska-Centre (ER-C) for Microscopy and Spectroscopy with Electrons & Peter Grünberg Institute (PGI): Microstructure Research Centre Jülich, 52425 Jülich, Germany

A R T I C L E  I N F O

Article history:
Received 28 August 2015
Received in revised form 11 May 2016
Accepted 5 December 2016
Available online 19 December 2016

Keywords:
Ion implantation
LiTaO$_3$ single crystal
Surface blistering

A B S T R A C T

Defects production and evolution in H and He ions co-implanted LiTaO$_3$ under different implantation order (H + He and He + H) are investigated. Rutherford backscattering spectrometry (RBS), infrared (IR) spectroscopy and transmission electron microscopy (TEM) are used to study the lattice damage, composition and structure change in the buried damage region. Obvious differences of ions aggregation mechanisms are found in H and He implanted LiTaO$_3$. Blistering or splitting of LiTaO$_3$ is more easily achieved in the case where He is implanted first compared to the reverse case. Significant damage enhancement and micro-fractures are observed in samples with He pre-implant. The dispersed damage in H-first sample is due to the destruction by He post-bombardment of H-clusters. This order effect indicates the strong aggregation and trapping ability of He ions and He bubbles. The effect of co-implantation parameters on the cleaving of LiTaO$_3$ is discussed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Lithium tantalite (LiTaO$_3$, LT) is an important material which possesses excellent electro-optic, ferroelectric and nonlinear optical properties [1,2]. It has a wide range of applications in function devices. In recent years more interest on LT devices is based on the use of crystal surface property and thin film structure, such as surface acoustic wave (SAW), ferroelectric and optical waveguide devices [3,4]. Single-crystal oxide thin films have great demand in integrated optical circuits and optoelectronics devices. This is not just because of the requirements of further miniaturization and integration of photonic devices on a single chip, but also the micro-structure of film with optimized shape and roughness could provide new opportunities to improve performances for crystal-based devices [5]. Conventional film growth processes show deficiencies when they are used in growth of oxide single crystal thin film with complex structures. Ion implantation based Smart Cut$^{TM}$ or CIS, provides a successful, practical and economical solution to this problem. At present there is a number of studies on fabricating thin oxide films (LiNbO$_3$, LT, BaTiO$_3$, etc) on insulator through H or He ion implantation followed by wafer bonding and thermal processing [6,7]. If appropriate implantation parameters are used, the aggregation of the implanted H or He forms sufficient internal pressure to lift-off of the overlying crystal layer. However, there are still some inherent problems with CIS technique, such as too many relevant variables (ion species, beam current density, temperature, ion fluence, crystal orientation and annealing condition etc.) related to smart cutting parameters, lack in repeatability and not being suitable for universal application, which restrict the application of CIS technique in preparing high quality single-crystalline thin films for many oxide crystals. For example, He implantation has been used as effective method to shear and transfer a thin LiNbO$_3$ layer from an implanted wafer onto a supporting wafer. While for LT, film obtained through CIS was only reported by H implantation [8,9]. Further attempts such as to decrease total implantation dose, to use other gas ions and to cleave crystal film by combining implantation with appropriate bonding techniques are being carried out in many important oxide crystals.

In CIS method thin film separation is based on the blistering. Blistering or exfoliation of crystal surface is multi-step phenomenon involving the combination of atomic mechanisms and macro mechanisms. Interaction of the implanted H and/or He ions with the host crystal lattice plays a key role in splitting and blistering. In some reports it is believed that the implantation generated defects are precursors to the formation of the extended H/He plates or micro-bubbles, which is the basis for buildup of internal pressure and ultimately exfoliation of the overlying layer [10,11]. However, blistering or exfoliation is a quite complex process, which has not yet been completely understood.

Some previous reports shows that H and He co-implanted silicon produces blistering at a much smaller total fluence than any
of the individual ion implantation alone [12]. Fluence reduction due to He and H sequential implant is attributed to He diffusion and being trapped in the hydrogen filled structures, where they are claimed to produce a much more effective pressure by He atom [13,14]. The synergistic effect of coimplantations, investigated by other groups, shows to be independent on the range of each ion species [15,16]. Compared with silicon thin film separation by H and/or He implantation, there are significantly fewer studies about ion slicing of LT and other oxide piezoelectric. In our previous studies we have investigated the process of blistering of LT by the sole ion (H or He) implantation [17,18]. However, the detailed mechanisms of ion slicing of LT, especially the aggregation mechanism of He and H ions in LT, are not clear. In order to investigate the synergistic effect of the co-implanted ions in the smart cutting process, different coimplantation conditions are performed in present experiment. We thereby can separate the relative contribution of H and He in coimplantation. In this study we focus on the effect of coimplantation on defects’ formation and ions evolution in defects.

2. Materials and methods

Congruent single-crystal Z-cut LT samples were implanted sequentially with H ions at energy 110 keV and He ions at 190 keV. Both ion beam current densities were kept at ~3 μA/cm² during implantation. Ion implantation was performed at room temperature. To minimize channeling effects, the surface normal was titled 7° from the incident ion beam. SRIM (Stopping and Range of Ions in Matter) simulations give an overlapped H and He ions stopping range of ~700 nm. In one case, samples were implanted with H ions first and then He ions. In another case, ion implantation order was reversed. Also the H/He ions fluence ratio was adjusted in two cases namely 1H:1He and 2H:1He. The total ion fluence range was (4–10) × 10¹⁶ ions/cm². Samples were characterized in detail both in the as-implanted and after thermal treatment. After ion implantation, crystal lattice damage was analyzed by Rutherford backscattering spectrometry (RBS). RBS measurements were performed using a 2.0 MeV ⁴He⁺ analyzing beam with a detector at a scattering angle of 165°. Selected samples were annealed in a heating process to observe blistering phenomenon through optical microscopy in ambient environment. High-resolution transmission electron microscopy (TEM) was used to characterize the detail structure change in the damage region. OH-absorption spectra were obtained by an infrared (IR) spectrophotometer at room temperature to analyze H-related substitution and interstitial defects.

3. Results and discussion

In the discussion that follows, we refer to different samples in the form of implantation fluence and order. Samples such as 3H + 3He means that 3 × 10¹⁶ ions/cm² H and 3 × 10¹⁶ ions/cm² He ions are sequentially implanted. Table 1 summarizes data on the observation of blistering for different implant conditions.

The simulated ion concentration and lattice damage profiles from both implanted ions are calculated using the SRIM code given in Fig. 1. The curves show an overlapped ion ranges in 500–800 nm from two species of ions. He implantation generate much high density of Frenkel defects compared to that of H implantation. In typical H or He implanted crystals, point defects and atoms displacement can induce a wide range of extended defects including dislocation loops, stacking faults, point defect clusters and even cavities or precipitates either in as-implanted or after post-implant thermal annealing [19,20]. In our previous studies we show that H implantation into LT results in the formation of H clusters. For He implanted crystal, some studies show that He ions tend to directly form micro-bubbles due to the low solubility and diffusion ability [21,22]. In the coimplantation process, defects and lattice disorder caused in first-step implantation can be modified in the subsequent implantation. The synergistic effect of two implanted ions will directly affect the formation of extended defects and lattice damage. Summary of the results can be clearly seen in Table 1.

It is well seen from Table 1 that, if He ions are implanted first, surface blistering or cracking occurs in most of the samples except the case of He fluence lower than 2 × 10¹⁶ ions/cm². In He-first coimplantation case surface blistering is induced in all the samples which have total ions fluence higher than 6 × 10¹⁶ ions/cm², this value is similar as the threshold fluence for blistering in only He-implanted LT. However, if samples are implanted in the reverse coimplantation order, e.g. H-first, surface blistering can hardly be achieved. Fig. 2 is a comparison of surface blistering, cracking and exfoliation from selected samples. For H-first implanted samples no surface blisters are observed, even for 5H + 5He sample with the total fluence of 1 × 10¹⁷ ions/cm². These results indicate that in the coimplantation process the synergistic effect of two implanted ions is not negligible. Selecting He or H as implanted precursor will have an important impact on the properties of defects and final film separation.

To analyze the damage or disorder properties in implanted LT, lattice damage induced by same fluence H and He but in different order is firstly analyzed using Rutherford backscattering spectroscopy in channeling mode (RBS/Ch). RBS/Ch is mostly sensitive to the atoms displaced from their crystalline position in any direction parallel to the sample surface. The Ta related part of the RBS/Ch spectra from samples in the virgin and coimplantation condition are plotted in Fig. 3. During implantation process the kinetic energy of the ion beam that hits the wafer is mostly transferred into heat and imposes a “dynamic annealing” for implanted ions and lattice damage. Actually, if implantation is carried out at high beam density the overall damage can be eventually alleviated due to such dynamic annealing effect. Results in Fig. 3 show that under the same total ion fluences the accumulated lattice damage in He-first sample is significantly larger than that of H-first sample. This means that the lattice damage produced in coimplantation is not

<table>
<thead>
<tr>
<th>Ratio</th>
<th>H-first Implanted</th>
<th>Annealed</th>
<th>He-first Implanted</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H:1He</td>
<td>3H + 3He</td>
<td>N</td>
<td>3H + 3He</td>
<td>C</td>
</tr>
<tr>
<td></td>
<td>4H + 4He</td>
<td>N</td>
<td>4H + 4He</td>
<td>C</td>
</tr>
<tr>
<td></td>
<td>5H + 5He</td>
<td>N</td>
<td>5H + 5He</td>
<td>B –</td>
</tr>
<tr>
<td>2H:1He</td>
<td>4H + 2He</td>
<td>N</td>
<td>2H + 4He</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>5H + 2.5He</td>
<td>N</td>
<td>2.5H + 5H</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>6H + 3He</td>
<td>C</td>
<td>3H + 6H</td>
<td>C&amp;E –</td>
</tr>
</tbody>
</table>

N represents no changes are observed.
B represents surface blistering.
C & E represents surface cracking and exfoliation.

Table 1
List of experimental parameters and corresponding annealing results.
the simply linear superposition of damages caused by single species ion implantation. The higher damage yield in He-first sample represents severe lattice disorder, which is usually associated with the presence of micro or nano-bubbles in crystal. Similar results have been reported in our previous work. Some experiments on He-implanted Si and LiNbO$_3$ also show that implantation-induced nanobubbles can induce a strong lattice deformation and lead to increase of the RBS/Ch yield [23,24]. In H-first samples, however, the lattice damage is significantly reduced. Even after consecutive He implantation, lattice damage does not show obvious increase. More unusual is that if taking the total ion dose into account, the damage yielded from H + He co-implanted sample (5H + 2.5He) is even lower than that of only H-implanted sample ($5 \times 10^{16}$ ions/cm$^2$). Our experimental results (listed in Table 1) show that most He-first samples exhibit blistering, cracking or exfoliation phenomena either in as-implanted or after annealing. While for H-first samples, no surface modification is observed, even after post-implant annealing.

To analyze these phenomena, we compare the co-implanted samples with the samples with only He or H-implantation. In He-implanted samples, surface blistering is induced during post-implant annealing process only in samples with He fluence higher than $5 \times 10^{16}$ ions/cm$^2$. In coimplantation process, He fluence needed for forming bubble or blistering is reduced. As is shown in Table 1, surface exfoliation can be induced in 3He + 3H sample, which contain only $3 \times 10^{16}$ ions/cm$^2$ He with follow-up $3 \times 10^{16}$ - ions/cm$^2$ H. This phenomenon can be explained by such a physical mechanism, i.e., the bubbles formed in He-first implantation grow with the help of post-implanted H. The small He bubbles are driven to coalesce to form big bubbles or fracture by capturing and absorbing H ions during the following H implantation. The dynamic annealing from implantation promotes the build-up of sufficient internal pressure in bubbles and to cause the liftoff of the overlying LT (Fig. 1(a)). For H-only sample, surface blistering is only observed in samples with H fluence higher than $6 \times 10^{16}$ - ions/cm$^2$, where H clusters can be observed in as-implanted samples according to our previous TEM results. However, different from the situation in H-only samples, blistering or exfoliation cannot be observed in H-first co-implanted LT, whether in as-implanted or annealed situation. Our interpretation of these results is that the formed H cluster is destroyed during the He post-implantation. Dynamic annealing resulted from He post-bombardment also can promote H ions diffusion. The pre-existing defects accommodate He ions and results in a relative high He solubility. These factors prohibit ions from aggregation and make the formation of H or He bubbles very difficult.

To verify above analyses we use TEM to observe microstructure of He + H and H + He samples. Figs. 4 and 5 present the cross-sectional TEM micrographs of 4He + 4H and 4H + 4He samples in as-implanted and annealed situation, respectively. Micro-cracks or platelets are formed in 4He + 4H as-implanted sample which can be clearly seen in Fig. 4. Linear defects (fracture) are concentrated in a very narrow range in depth. Size of some defects is in hundreds nanometers, one order of magnitude larger than the typical sizes of platelets in He as-implanted LiNbO$_3$ [22]. It supports our analyses that He bubbles grow and coalesce during implantation by capturing and absorbing post-implanted H. It can be inferred that surface exfoliation sets off mostly along the linear fractures in these samples during annealing treatment. Since dynamic annealing effect of subsequent H implantation promotes
defects diffusion and lattice restoration, obvious clusters or scattered defects are not found in surrounding area, see Fig. 4(a). This analysis can be used to explain most of the phenomena in He-first co-implanted samples given in Table 1. For the sample with He fluence lower than $2.5 \times 10^{16}$ ions/cm$^2$, ion concentration is too small to form an effective aggregation centre or bubble. Therefore no surface modification can be induced.

Fig. 5 is a cross-sectional TEM image from H first as-implanted and annealed sample. A total dispersed damage region with depth of $\sim 730$ nm is shown in Fig. 5(a). The range of lattice damage is consistent with the SRIM calculations (Fig. 2). From Fig. 5(a) it can be seen that the implanted region is clearly divided into three parts: an almost undisturbed $\sim 200$ nm width near surface region; obviously disturbed region from 200 to 730 nm and the bulk substrate. Every part exhibits a relative uniform profile in as-implanted sample. Even for disturbed region from 200 to 730 nm the crystal disorders appear to be uniformly distributed in depth. It is quite different from the H-only sample, where TEM result shows a dense lattice disorder with platelets or clusters at the depth of ion range [17]. He post-bombardment breaks H aggregation apart and promotes the diffusion of H. These dispersed defects result in a broader damage region, which can be observed in Fig. 5(b). After annealing, lattice disorder becomes concentrated and more obvious in the vicinity of implantation depth (Fig. 5(c)). Some damaged lattices get partially recovered in the near surface region. But lattice disorders are still distributed over a relatively wide range $\sim 300$ nm. Different from the circle or oval-shaped clusters or platelet found in most H or He implanted crystals, sheet-like and linear dislocations are observed in annealed H + He sample. These defects or disorders may represent the structures of twinning, boundary between different domain structures or dislocation loops, which is the result of high concentration of clusters induced local, buried compressive-strain filed [21]. One of enlarged view of lattice disorder shown in Fig. 5(d) exhibits the possible local twin band or dislocation loop. Some linear defects extend even to sample surface Fig. 5(c), they are related directly to the appearance of surface cracking shown in Fig. 1(b).

In addition to the effect of dynamic annealing on defects formation and distribution, chemical bonding between implanted ions and constitution atoms should also be taken into consideration in coimplantation process, because it has a direct impact on accumulation of implanted ions, especially for H aggregation. H ions have much stronger chemical activities compared to He and tend to form relative stable bond in oxide crystal, such as O-H structure. To investigate the chemical interaction of implanted H in LT, infrared spectra of co-implanted LT are measured and given in Fig. 6.

Similar as virgin LT crystal, several typical OH absorption peaks from 4H + 4He and 4He + 4H implanted samples can be found in the wavenumber range from 3450 to 3520 cm$^{-1}$. It has been reported that in most cases the in situ doped H ions will replace the Li ions or attach with O-O bonding by positioning themselves at the interstitials [25–27]. The typical OH absorption peak is at around 3484 cm$^{-1}$, which is marked by blue line in Fig. 6. However, if we compare the measured spectra from virgin sample with co-implanted sample, some subtle difference can be noticed. By deconvoluting the measured profile (marked by black line for measured profile and cyan line for cumulative fit, respectively), each spectrum can be decomposed into three components, labeled as S ($3462$ cm$^{-1}$), M ($3475$ cm$^{-1}$), and L ($3484$ cm$^{-1}$) in the sequence of wavenumber. It has been reported that the low wavenumber $3462$ cm$^{-1}$ peak S is corresponding to protons directly substituting Li ions [28,29], because H$^+$ ions are easily attracted by the Li vacancy ($V_{\text{Li}}$) defects due to the different electrical charges and formation of ($V_{\text{Li}}$)–OH complexes. While the middle and high wavenumber ($3475$ cm$^{-1}$ and $3484$ cm$^{-1}$) absorption peaks M and L are corresponding to protons occupying defects $V_{\text{Li}}$ near Ta antisite ($Ta_{\text{Ta}}^{\text{Li}}$) [30–32]. As is shown in Fig. 6, the area under the absorbing profile slightly increases after implantation. Obvious red-shift of absorption peak can be found in implanted sample. Different from the situation in virgin sample, where L peak at $3484$ cm$^{-1}$ dominates almost the whole spectrum, S peaks (marked by red line) are obviously enhanced in implanted samples. Although the spectra show similar profiles in both co-implanted samples, the S peak area is much larger in H-first sample compared to He-first sample (1.04 vs. 0.57). It can be explained that in H-first implantation Li atoms are kicked out of their lattice sites because of a near elastic collision between H and Li ions. The substitution of H for Li can be promoted by dynamic annealing effect in the following He post-implantation. In this case interstitial H ions are dri-
To directly substitute Li rather than be attached to vacancies. The (V_Li)OH absorption band 3475 cm^{-1} in implanted samples is also significantly enhanced compared with that of virgin crystal. This increment in M peak, accompanied by the decline of L peak at 3484 cm^{-1}, represents a modified local defect environment caused by implantation, which is dependence on a synergistic result from two kinds of ion implantations.

In H and He coimplantation process, mechanism of defects formation becomes different and complex due to the synergistic interaction of two different implanted ions. This makes it possible to optimize the conditions of CIS by adjusting implantation and annealing parameters. Further studies are in progress.

4. Conclusion

We have studied H and He ions co-implanted LiTaO_3 under different implantation orders and fluence ratios. Surface blistering is induced more easily in He-first implanted samples because He bubbles are driven to coalesce by post-implanted H and grow by absorbing the H ions. In H-first samples, H ion aggregation is disturbed and inhibited by the following He implantation. A disperse disorder distribution is caused in implanted range, which makes ions aggregation more difficult. Defects and lattice damage properties are analyzed based on our RBS/CH measurement, TEM views and IR absorption spectra.

Acknowledgments

This work was supported by the National Nature Science Foundation of China (Grant No. 51272135 and 11475105) and the State Key Laboratory of Nuclear Physics and Technology, Peking University.

References


Fig. 6. Normalized OH absorption spectra from virgin sample and samples with H and He ions co-implantation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)