Study of the effect of H implantation and annealing on LiTaO₃ surface blistering

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LiTaO₃ samples are implanted by 120 keV hydrogen ion with different fluences at room temperature. H⁺ concentration and distribution is detected using Elastic recoil detection. Experimental results show that the threshold fluence for blistering in LiTaO₃ surface is 6 × 10¹⁶ ion/cm². Surface blistering phenomenon is studied by using optical microscopy, Rutherford back scattering spectrometry, transmission electron microscopy and atomic force microscopy. Bubble growing and surface blister’s dependence on annealing process is observed and analyzed. The critical internal pressure and stress of surface blistering in H⁺-implanted LiTaO₃ is derived based on theoretical model and experimental results. Gibbs free energy and cavity critical radius are introduced to explain the blister shrink and rupture observed in the experiment.

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1. Introduction

Lithium tantalite (LiTaO₃) is a typical ferroelectric and piezoelectric material, with a large number of applications in optical, electro-optical and piezoelectric devices due to its excellent electro-optical and nonlinear optical properties [1–4]. It is also important in applications of surface and thin film devices such as surface acoustic wave (SAW) and optical waveguide devices. Manufacturing such device with limited size single crystal film is needed to meet the requirement of optoelectronic integration and miniaturization of photonic devices. Many techniques, such as chemical vapor deposition, RF sputtering, molecular beam epitaxy, sol–gel, and pulsed laser deposition have been used to produce single-crystalline thin films. However, all these techniques have difficulty in producing oxide single crystal film with high quality. It is because that the optical oxide crystals usually have complex lattice structures and the lattice mismatching between film and substrate seriously affects the quality of the epitaxial film. More recently, crystal ion slicing (CIS) in combination with wafer bonding techniques has emerged as a very promising technique for fabrication of single crystalline ferroelectric thin films [5,6]. In this method, hydrogen or helium ions are implanted into oxide crystal with enough ions fluences, layer splitting or layer exfoliation being achieved in the following annealing treatment. It is first introduced as a highly effective silicon layer transfer method for the fabrication of silicon-on-insulator (SOI) wafers [7]. Crystalline LiTaO₃ films obtained by H-ion implantation have been reported in several references [8,9]. The ion-cut process results from the micro-cracking at implantation depth due to ions aggregation. It is closely related with the blistering phenomenon on crystal surface [10], which has been considered to be controlled by the implantation-induced damage during implantation and after post-implantation annealing. H-induced surface blistering has been observed in several semiconductors, such as Si and GaN etc [11,12]. However, few reports are found referring to blistering process in H-implanted LiTaO₃ crystal. As is known that the blistering process assists in defining the implantation and annealing parameters for successful ion-cut of crystal, and therefore the mechanism of blistering needs a further study in order to provide detailed insight of layer splitting in LiTaO₃. In our present experiment, 120 keV H⁺ ions were implanted into LiTaO₃ with different fluences at room temperature. The lattice damage and the blistering/flaking phenomena in as-implanted and annealed LiTaO₃ crystals are investigated. The effect of pressure and stress within H₂ bubbles on surface buckling is discussed in the framework of Föoppl-von Karman (FvK) theory [13]. Based on the measured results, the critical internal pressure and stress for blistering in H⁺ implanted LiTaO₃ is estimated.

2. Materials and methods

Z-cut congruent LiTaO₃ single crystal wafers, with the size of 10 × 5 × 1 mm³, are implanted by 120 keV H⁺ with different...
fluence ranging from $5 \times 10^{16}$ to $8 \times 10^{16}$ ions/cm$^2$. During the implantation, the sample surface is tilted 7° off the ion beam direction to minimize the channeling effect. SRIM (Stopping and Range of Ions in Matter) is used to simulate the ion distribution and damage profile. The ion beam current density is kept at 3 μA/cm$^2$. After implantation, the crystal lattice damage is analyzed using Rutherford back-scattering/channeling spectrometry (RBS/Ch). The RBS/Ch measurements are performed using 2.0 MeV $^4$He$^+$ and the back-scattering ions are detected with a surface barrier detector at a scattering angle of 165°. Lattice damage profiles are extracted by using a multiple-scattering dechanneling model, which is based on Feldman’s procedure and is applied for all target elements in the crystal [14]. Elastic recoil detection (ERD) analysis is performed to measure the hydrogen concentration and distribution. A 4.5 MeV $^4$He$^+$ analyzing beam is incident on a sample with 75° from the surface normal. To avoid detection of forward-scattered He particles a 23 μm thick Mylar foil is positioned between the sample and the hydrogen detector during ERD measurement. Surface morphology of H-implanted LiTaO$_3$ is observed by atomic force microscopy (AFM) in the tapping mode. The blistering process versus annealing temperature and time is examined by using an optical microscopy (OM) with a hot plate. The post-implantation sample is heated gradually from room temperature to 600 °C, while the OM monitors the change in LiTaO$_3$ sample surface.

3. Results and discussion

Fig. 1(a) shows the RBS/Channeling spectra of samples implanted with ion fluence ranging from $5 \times 10^{16}$ to $8 \times 10^{16}$ ions/cm$^2$. For comparison, the spectra in channeling and random condition of a virgin LiTaO$_3$ crystal are also given. Very similar lattice damage profiles are induced after H$^+$ implantation with different ion fluences. A small distinguishable peak in backscattering yield at channel 250 comes from the direct scattering of He$^+$ ion from the displaced atoms in LiTaO$_3$ crystal. Fig. 1(b) shows the damage comparison between the experimental and the simulation result for LiTaO$_3$ implanted by 120 keV H$^+$ ion with fluence of $5 \times 10^{16}$ ions/cm$^2$. The extraction of lattice damage only considers the Ta sub-lattice and does not represent damage in the O and Li sub-lattices. It can be found that hydrogen ion implantation causes about 12% lattice disorder at a depth of ~750 nm from the sample surface.

H$^+$ ions concentration and distribution are detected by using ERD analysis. Fig. 2 shows the result from sample implanted with $5 \times 10^{16}$ and $6 \times 10^{16}$ ions/cm$^2$ H$^+$. In as-implanted $5 \times 10^{16}$ ions/cm$^2$ sample the peak H$^+$-concentration is 0.3 at.%, much lower than the predicted value of 1.8 at.% according to SRIM simulation. After annealing, hydrogen concentration decrease to 0.2 at.%. For $6 \times 10^{16}$ ions/cm$^2$ H$^+$-implanted sample, the corresponding values are 0.6 at.% and 0.28 at.%, respectively. This result is significantly different with H$^+$ implanted Si crystal, where the measured H$^+$ ions concentration shows a good agreement with the simulation results [15]. This difference should be mainly due to the different diffusion ability of H$^+$ ions in LiTaO$_3$ and Si crystal. H$^+$ ions diffuse more easily in LiTaO$_3$ crystal via lattice defects or by substituting Li$^+$ ions [16]. In the present experiment, H$^+$ diffusion is enhanced because of a dynamic annealing effect during implantation. It arises from the sample heating caused by implantation at high beam current density (3 ~ 4 μA).

For H$^+$-implanted LiTaO$_3$, there are no reports available which can explain the relation between the real H$^+$ concentration and the implantation fluences. If we use the values from the semiconductor material as reference, the threshold implantation fluence for surface blistering in H$^+$ implanted LiTaO$_3$ may be underestimated. After implantation, no surface blistering is observed for all the as-implanted samples. During the post-implantation annealing process, the as-implanted samples are placed on a hot plate which can be continuously heated from 200 to 600 °C. The experimental parameters and results are summarized and given in Table 1. For $5 \times 10^{16}$ H$^+$/cm$^2$ implanted sample, no blistering phenomenon is observed throughout the whole annealing process, even after it is annealed at 600 °C for 60 min. Blistering occurs in the surface of $6 \times 10^{16}$ H$^+$/cm$^2$ implanted sample after annealing...
at 250 °C for 10 min. Extending annealing time and increasing temperature to 400 °C, blistering becomes less visible in observation by OM. Flaking is not observed. For samples implanted by 7 × 10^{16} and 8 × 10^{16} H⁺/cm² implantation, surface blistering arises both at 200 °C but after different annealing duration.

Fig. 3(a) shows the surface blistering in 7 × 10^{16} H⁺/cm² sample after annealing at 200 °C for 44 mins. To observe how the blistering growing, sample is continuously annealed at this temperature for more than two hours. Fig. 3(b) exhibits the surface blistering condition after different annealing time. It can be found that with the extending of annealing time, surface blisters originally increase to a certain extend and then begin to shrink. It is very similar to the blistering phenomenon in 6 × 10^{16} H⁺/cm² sample. It means that the pressure inside the blisters does not exceed the fracture toughness of the LiTaO₃. Flaking is observed in 8 × 10^{16} H⁺/cm² samples after annealing at 200 °C for 90 mins. Fig. 4 shows the blistering evolution in this sample during annealing at 200 °C. The inset AFM images show the corresponding sample surface morphology. The thickness of flaking is about ~ 800 nm, which is consistent with the depth of lattice damage peak.

Fig. 5 gives a XTEM image of the implanted region in 7 × 10^{16} H⁺/cm² as-implanted sample. Fig. 5(a) shows a ~ 700 nm region of less dense damage followed by a ~ 100 nm tail region of dense damage. This tail region consists of clusters or rounded strain centers whose lateral size is between 10 and 20 nm, see Fig. 5(b). By comparison with other experimental results in H-implanted Si, GaN and LiNbO₃, these clusters consisted of platelets, bubble-like defects and strain centers from lattice disorder. They will be act as nucleation centers for the agglomeration of diffusing H in the following annealing treatment. If the density of clusters is high enough, small hydrogen bubbles will grow in size via Ostwald ripening. Annealing at higher temperature leads to an increase of the pressure within these bubbles and platelets and therefore the formation of micro-cracks in damage region. When the internal pressure of the micro-crack exceeds crack stability pressure, micro-cracks become movable and overlap between adjacent micro-cracks within a narrow width near to the H-concentration peak in the dense damage band [8,17]. Blistering/splintering is the result of the coalescence of the micro-cracks in damage region [18].

To investigate the relationship between H⁺ fluence and internal pressure of hydrogen bubbles in H⁺-implanted LiTaO₃, the surface energy of LiTaO₃ is estimated according to L.B. Freund’s theory [19]. Several theoretical models have been given to estimate the threshold fluence for blistering on ion implanted crystal. L.B. Freund calculated the internal pressure of hydrogen gas induced surface blistering in a considered nominally elastic material. By assuming that the radius a of the micro-cracks (or blisters) is small compared to the thickness h (the layer above the micro-cracks), his study gives the formula for minimum value of implantation fluence

\[ J_{\text{min}} = \frac{8}{3} \frac{\gamma}{kT} \]  

(1)

In the formula, \( \gamma \) is the surface energy density, k is Boltzman’ constant and T is absolute temperature. In our experiment, the blistering occurs on the sample with minimum fluence of 6 × 10^{16} ions/cm² at annealing temperature \( T = 250 \) °C. According to Eq. (1), the \( \gamma \) can be estimated. However, not all the implanted atoms contribute to the growing of the micro-cracks according to our ERD measurement. Some will have diffused out of the layer during the implantation process. Supposing that all the detected hydrogen ions in our ERD measurement are incorporated into micro-cracks growing, it means that only 27% of total implanted hydrogen is available. Thus the surface energy density \( \gamma \) of LiTaO₃ is estimated to be 0.44 J/m² under the present implantation condition.

Similar to the situation in H/He ion implanted Si, GaN and other materials [20–22], micro-cracks result in buckling in H⁺-implanted

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fluence (× 10^{16} ions/cm²)</th>
<th>Annealing (°C)</th>
<th>Blistering Temperature (°C)</th>
<th>On-set Time (min.)</th>
<th>Flaking</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>200 − 600</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>200 − 400</td>
<td>250</td>
<td>10</td>
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</tr>
<tr>
<td>3</td>
<td>7</td>
<td>200 − 400</td>
<td>200</td>
<td>18</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>200 − 400</td>
<td>200</td>
<td>10</td>
<td>Yes (200 °C)</td>
</tr>
</tbody>
</table>

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Fig. 3. Optical microscope images of the blistering surface in 7 × 10^{16} H⁺/cm² implanted LiTaO₃ (a) sample surface after annealing at 200 °C for 40 minutes; (b) the condition of surface blistering in a selected area in (a) after annealing at 200 °C for different annealing duration.
LiTaO$_3$ surface layer. According to elasticity and linear fracture mechanics concepts, an overpressurized H-crack can be defined as a Griffith crack structure. Based on this theoretical model, the buckled layer of H$^+$-implanted LiTaO$_3$ is schematically shown in Fig. 6. In this model the “pancake” shape cavity on sample surface is filled with hydrogen gas and encapsulated by LiTaO$_3$ film with thickness around 800 nm (consistent with TEM results). As a general rule, the plane of an inclusion that is normal to smaller elastic modulus will have a larger area than for the projected area in other directions [23]. The average deflection $d$ of the buckled layer and the radius of craters $a$ are measured by AFM to be 50 nm and 5 $\mu$m, respectively (Fig. 4).

The buckling phenomenon of thin films has been extensively analyzed in FvK theory [24,25]. The compressive stress in the initial flat thin layer is defined as $r_0$, which is taken to be positive in compression. The stress in the buckled part is labeled as $r_{xx}$. If the layer of thickness $h$ is already delaminated over a distance $2a$, within the framework of FvK’s theory, the vertical displacement $w$ (inner crack vertical displacement in Fig. 6) of the layer must satisfy [26]

$$\frac{\partial^4 w}{\partial x^4} - \frac{h}{D} \frac{\partial^2 w}{\partial x^2} = \frac{\Delta p}{D}$$

The bending stiffness $D$ is defined as $D = h^3 E/12(1 - \nu^2)$, with $E$ the Young modulus and $\nu$ Poisson ratio of the layer. The pressure mismatch is defined as $\Delta p = p_{\text{int}} - p_{\text{out}}$, with $p_{\text{int}}$ and $p_{\text{out}}$ the internal pressure in the cavities and the pressure acting on the free surface of the materials, respectively.

It is found that the shape of the buckle depends on the state of stresses $\sigma_{xx}$ in the buckle. If a critical pressure variation $\Delta p_c$ is defined as the pressure mismatch when the buckled film is completely relaxed ($\sigma_{xx} = 0$), then we have [25],

$$\Delta p_c = \sqrt{\frac{105E}{16(1 - \nu^2)} \left(\frac{h}{a}\right)^3} = \frac{24D}{\sigma_0^a} \delta_c$$

with $\delta_c$ and $\sigma_0^a$ the associated maximum deflection of the buckle and the associated internal stress, respectively. The threshold $\sigma_0^a$
of the internal stress in the planar layer obtained for $\sigma_{xx} = 0$ is given from Eq. (3) by [27]

$$\sigma_0^2 = \frac{64E}{105(1 - \nu^2)} \left( \frac{d}{a} \right)^2$$  \hspace{1cm} (4)

Substituting $E = 205$ GPa, $\nu = 0.25$ for LiTaO$_3$ crystal [28] into above Eq and let $a = 5 \mu m$, and $d = 50$ nm, the critical pressure mismatch $\Delta p_0$, and threshold tensile stress $\sigma_0^2$ are calculated to be $\sim 22$ MPa and $\sim 17$ MPa, respectively. The two values are corresponding to the threshold internal pressure and stress to trigger the micro-cracking in LiTaO$_3$ crystal. They are much larger than the normal external pressure ($p_{\text{ext}}$) of $\sim 0.1$ MPa acting over LiTaO$_3$ crystal surface, but much lower than the actual internal pressure in H$_2$ blisters. The inner cavity pressure can be estimated through the relationship of Gibbs free energy and the critical radius of cavities. If Gibbs free energy is expressed as a function of radius $a$ and temperature $T$, the total free energy of a growing hydrogen blister can be written as [28]

$$G(a, T) = W(a) + U(a) + H(a, T)$$ \hspace{1cm} (5)

where the external potential energy $W$ is the hydrogen pressure working through the crack face displacement; $U$ is the elastic strain energy of bulk LiTaO$_3$ around a blister and $H$ is the crack surface energy of a blister. At the condition for cavity nucleation, $dG/aT/da = 0$, one can obtain the critical radius as [29]

$$a_{\text{cr}} = \frac{\pi \gamma(T)E}{0.18p^2(1 - \nu^2)}$$ \hspace{1cm} (6)

In Fig. 7, the Gibbs free energy and the critical radius for each inner pressure are shown. The free energy for cavity nucleation becomes maximal at the critical radius. If the radius is smaller than the critical radius, $dG/da$ is larger than zero. Here, the blister is unstable and shrinks away if an additional driving force is not present, which is the case we observe in sample 2# and 3#. When a blister’s radius is larger than the critical radius, it grows indefinitely until the blister ruptures or coalescence with another blister intervenes. In Fig. 4(b), we can obtain the radius of crater around 10 ~ 15 $\mu m$. This value lies in the range of critical radius of blisters at internal pressure from 400 to 500 MPa in Fig. 7. It represents an actual internal pressure of H$_2$ blister in H$^-$-implanted LiTaO$_3$. A lower internal pressure corresponds to a much larger rupture radius, which is not consistent with our experimental results. Hydrogen induced blistering is a chemical as well as a physics process. It depends not only on the implantation parameters but also the difference on elastic properties and surface energy of material. Our experiment shows a larger critical radius in H$^-$-implanted LiTaO$_3$ than that of H$^+$-implanted BaTiO$_3$ (forms $\sim 6 \mu m$) and H$^-$-implanted Si ($\sim 1.5 \mu m$) at the same internal pressure of 500 MPa. From Eq. (6) it can be found that the critical radius is proportional to the surface energy density $\gamma$, which is 440 mJ/m$^2$ according to our calculation. This value may be overestimated because we have assumed that all the ERD detected hydrogen ions participate in the cavity growing. For H$^-$-implanted Si it was reported that the available H is only 30% as measured by mass spectrometry [30]. If such modification is also introduced into H$^-$-implanted LiTaO$_3$ crystal, the actual internal pressure in H$_2$ blister and critical radius should be smaller than the present results.

4. Conclusion

The dependence of the H$^-$-implant induced LiTaO$_3$ blistering on implantation fluence has been investigated in this work. Real H$^+$ concentration and distribution is detected by ERD. Surface blistering phenomena are monitored through OM in a dynamic annealing process from temperature 200 to 600 $^\circ$C. The microstructure in damage region is investigated using TEM measurement. According to the threshold H$^+$ fluence of $6 \times 10^{16}$ ion/cm$^2$ and the actual H$^+$ concentration from ERD measurement the surface energy density of LiTaO$_3$ crystal is estimated. The physical mechanism of the surface blistering, as well as the critical pressure mismatch and stress for H$^-$-implanted LiTaO$_3$ blistering are discussed and calculated. Gibbs free energy and critical radius are introduced to explain the blister shrink and rupture observed in the experiment.

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