CHAPTER 4

INFLUENCE OF SWIFT IONS AND PROTON IMPLANTATION ON THE FORMATION OF OPTICAL WAVEGUIDE LAYER IN LITHIUM NIOBATE CRYSTAL

4.1 INTRODUCTION

Integrated optics is a discipline that not only deals with classic optics but also the overlap of electronics and optics. There are wide range of related techniques, such as electro-optics, optoelectronics, nonlinear optics, optical communications and lasers. These are very important and popular in aspects of both science and technology (Iizuka 2002). The subject of integrated optics bridges many research fields with the waveguide technology to offer a more compact platform, and it is also regarded as the basis of modern optical communications. Optical waveguide is one of the basic components in integrated optics and optoelectronics. Optical waveguides are fabricated in the materials having a region with high refractive index surrounded by region with lower refractive index. Such type of structure allows the light confinement by means of total internal reflection occurring at the junctions between the boundaries of guides and claddings. They can confine light propagation within small volumes in one or two dimensions i.e. a planar structure for one dimensional (1D) and a ridge structure for the two dimensional (2D).

In waveguide preparation process by ion implantation, some properties of target materials can be considerably improved relative to those
of the corresponding bulk material. For example, laser generation in waveguide possesses a lower pumping threshold and photorefractive waveguides usually have faster response than the bulk components by ion beam process (Mackenzie 2007). The waveguide structure by implantation is small in size, which allows for the fabrication of compact optical circuits or chips for easy combination with other optical components for several applications. The small size of optical waveguide structures offers high light intensities produced by very low powers, in addition to that the nonlinearities or laser action in the guiding layer may be more efficient than those in bulk material. Also the components based on waveguides may be connected together with optical fibres easily. This is because of the dimension of waveguides are directly compatible with fibres used in telecommunication applications, in which optical waveguides are used often as amplifiers, signal switches and modulators (Murphy 1999).

There are several techniques for fabricating waveguide structures in optical materials such as diffusion of metal ions (Jaque et al 2007), sol gel (Nashimoto and Cima 1991), ion exchange (Rodríguez et al 2007), ion implantation (Chen et al 2007), direct UV laser writing (Mailis 2003) and pulsed laser deposition (Wang et al 1998) or combination of a few of the above mentioned methods. Among these techniques, ion implantation possesses one of the most advantageous characteristics, that is, the wide applicability of materials with low degradation of opto-electronic properties, transmission of the target material and without introducing detrimental tilt of the optical mode polarization plane.

4.2 INFLUENCE OF PROTON AND SWIFT ION BEAM ON LiNbO₃ SINGLE CRYSTAL

A large number of optical materials have been used as substrates for wave guiding devices, including semiconductors, oxide crystals, glasses
and polymers (Buchal 1995). Although the waveguides in optical materials have been studied for several years, there is no unique explanation for all materials, because of the diversity of configuration and properties. However, the simple model, which was first proposed by Townsend 1994, seems to be a reasonable explanation at least for most optical crystals. When implantation of light ions at energies of several MeV are performed, most of the lattice damage occurs at the end of the ion track inside the substrates, which results in a decrease of physical density by means of volume expansion and hence a reduced refractive index of an optical barrier. Such an optical barrier confines the input light in a narrow layer with relatively high refractive index between the barrier and the crystal surface, forming an optical waveguide. The tunnelling effect may take place when the optical barrier is not adequate, (i.e) high or wide leads to leakage of light energy (Pogossian 2003).

Lithium niobate (LiNbO$_3$) single crystals are key material for fabrication of integrated optical devices due to its superior electro-optic, nonlinear optical coefficients, and high Curie temperature ($T_c$) (Fu et al 2003). Since the invention of LiNbO$_3$ in 1960, much attention has been directed towards this crystal family, and many of its characteristics have been analyzed well. It can be used in modulators, surface acoustic wave devices and for frequency doubling. The commercially available LiNbO$_3$ has a congruent composition with a number of intrinsic defects. When incorporated with certain extrinsic ions, for example, Mg or Cu, Ti or Ni and Er or Tm ions, lithium niobate exhibits remarkable photorefractive properties, optical waveguide and laser gain media respectively. In addition, ion species such as Fe and Mg can also be doped into LiNbO$_3$ for the application of holographic storage and photorefractive damage resistance respectively. In addition, LiNbO$_3$ can be easily grown in large scale, big crystals via the well known Czochralski method, which makes LiNbO$_3$ cost effective for various opto-electronics applications. Several waveguide fabrication processes, viz., proton
exchange, titanium diffusion and light (H or He) ion implantation, have been
developed to obtain integrated optical circuits in LiNbO₃. Proton exchanged
waveguides suffer from degradation of nonlinear optical figure of merit
(Suhara 1989). Properties of waveguides developed by ion diffusion process
strongly depend on exchange conditions as well as the quality of the substrate
material (Avrahami and Zolotoyabko 1996). However, the possibility of
introducing ion impurity at low temperature with accurate control of the
energy, fluences, depth, and lateral concentration of the dopants, which are
sensitive to the waveguide structures, make the ion implantation process to be
an extensively attractive technique for waveguide fabrication (Benti 2005).

Ion implantation is a mature technology for semiconductor
technology and widely used in the optical communication devices. Ions at
energies above 100 keV are likely to penetrate into the substrate rather than
target sputtering. Ion fluence of the order of 10¹⁶ ions/cm² or higher are
necessary during light ion implantation (H or He) to form waveguides. An
optical barrier will be built up on the material on implantation at the end of
the ions trajectory. Ions with energies greater than 1 MeV/amu can be called
“swift” ions; in some cases of material modification, the minimum threshold
value is ~ 0.1 MeV/amu. There is an increasing demand for such high
energetic ion beams for physics as well as material science, particularly in the
case of heavy ions. In these cases, the electronic energy created by the
irradiation is dominant over the nuclear damage along the track of the incident
ions. Peithmann et al (2006) used Swift light ions of He at energies greater
than 40 MeV to irradiate optical crystal for change of refractive index for
optical waveguides. Table 4.1 summarizes the various ion beam techniques
that are generally used to modify the LiNbO₃ crystals, including their main
parameters and the main effects of these methods have on the target materials.
Since the first proton implanted waveguide in fused silica reported by Schineller et al (1968), waveguides have been so far fabricated in more than 100 optical materials by implantation of various ions at the energies of several keV upto several MeV. Proton containing lithium niobate optical waveguides are widely used in integrated optics. The proton ions influence several properties in LiNbO₃ crystal such as increase of the extraordinary index values, nearly step-like index profile and higher threshold of optical damage which are favourable for guided wave optical technology. To achieve optimal tailoring of the guided wave optical parameters for specific applications, detailed knowledge of relation between structural, optical and surface properties of the implanted layers is important.

Table 4.1  Techniques related to energetic ion beams and their main parameter

<table>
<thead>
<tr>
<th>Ion beam techniques</th>
<th>Typical ion energy range</th>
<th>Main effects</th>
<th>Remarks related to LiNbO₃ crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion beam deposition</td>
<td>10–100 eV</td>
<td>Film deposited on the target</td>
<td>Not applicable for waveguide formation due to poor qualities</td>
</tr>
<tr>
<td>Ion implantation</td>
<td>100 keV–6 MeV</td>
<td>Implantation into target, causing nuclear and electronic damages</td>
<td>Nuclear damage creating buried amorphous layer</td>
</tr>
<tr>
<td>Swift Ion irradiation</td>
<td>12 MeV–GeV</td>
<td>Implantation into target, causing nuclear and electronic damages; electronic damage is dominant over the nuclear one</td>
<td>Electronic damage causing buried amorphous layer even at low dose; threshold of electronic stopping power of complete amorphization ~ 5 keV/nm</td>
</tr>
</tbody>
</table>
Attempts were made to implant protons (120 keV ions) on congruent Ti:LiNbO₃ (Ti doped), to irradiate lithium (50 MeV ion) on congruent Ti:LiNbO₃ (Ti doped) and also on the proton implanted Ti:LiNbO₃ samples. The purpose of 50 MeV Li³⁺ ions is to recover some loss of Li ions from the implanted region of LiNbO₃ after ion implantation. High resolution x-ray diffraction (HRXRD) was used to observe the changes in lattice strain profile due to implantation and irradiation processes. HRXRD results measurements were compared with the atomic force microscopy (AFM) images. In addition, optical and spectroscopic analyses were made for the implanted as well as irradiated samples to optimize the conditions (energy, fluences, etc.) for the waveguide layer development.

4.3 EXPERIMENTAL PROCEDURE

Single crystals of LiNbO₃ (pure and doped with 5 mol % titanium) were grown from melts with the congruent composition (48.6 mol % Li₂O). The crystals using “Z” cut seed were grown by conventional Czochralski method. Specimens of thickness of ~ 0.7 – 0.8 mm from the crystal boule were sliced perpendicular to the crystallographic c axis. Ion implantation (proton ions) and irradiation (Li ions) were carried out on the polished wafers of lithium niobate samples at Inter-University Accelerator Centre, New Delhi using a LEIBF and 15UD pelletron accelerator, respectively. The vacuum in the radiation chamber during the experiment was about 8×10⁻⁷ mbar. Protons (H⁺) of energy of 120 keV and fluences of 1×10¹⁵, 1×10¹⁶, and 1×10¹⁷ ions/cm² were used for implantation. Lithium (Li³⁺) ions of energy of 50 MeV with fluences ranging from 1×10¹¹ to 1×10¹³ ions/cm² were used during irradiation. To avoid charge pileup, the beam current was maintained as ~ 10 nA for implantation and 0.5 nA for irradiation processes. The lattice damage induced by ion implantation is considered to be the main reason for change in index profile in the LiNbO₃ waveguide. There are two
different types of damages (Bentini et al 2004) produced by ion implantation: Near surface damage generated by electronic stopping, which induces an increase in extraordinary refractive index and at the end of ion track, and damage correlated to nuclear collision cascades, which decrease the extraordinary refractive index values. The depth profile and other parameters of proton ions and lithium ions in LiNbO$_3$ lattice have been simulated using stopping and ranging of ions in matter (SRIM 2006) code (Table 4.2).

Table 4.2 Summary of implantation and irradiation parameters in LiNbO$_3$ (Z-cut) single crystal

<table>
<thead>
<tr>
<th>Ion</th>
<th>Proton ($H^+$)</th>
<th>Lithium ($Li^{3+}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>120 keV</td>
<td>50 MeV</td>
</tr>
<tr>
<td>Projectile Range ($R_p$) $\mu$m</td>
<td>0.812</td>
<td>225.7</td>
</tr>
<tr>
<td>Longitudinal straggling ($\Delta R_p \parallel$) $\mu$m</td>
<td>0.1453</td>
<td>9.26</td>
</tr>
<tr>
<td>Lateral straggling ($\Delta R_p \perp$) $\mu$m</td>
<td>0.1682</td>
<td>7.20</td>
</tr>
<tr>
<td>$(dE/dx)_n$ eV/ Å</td>
<td>$2.122 \times 10^{-2}$</td>
<td>$7.521 \times 10^{-3}$</td>
</tr>
<tr>
<td>$(dE/dx)_c$ eV/ Å</td>
<td>13.96</td>
<td>13.62</td>
</tr>
</tbody>
</table>

Figures 4.1(a) and (b) show the projected ion range and vacancy distribution in CLNT5 crystal simulated by the Monte Carlo programme of Transport of Ions in Matter (TRIM) for $H^+$ ions and $Li^{3+}$ ions respectively. Here 99999 ions were used to simulate these graphs for better results. For $H^+$ ion implantation, vacancies were created along the proton path and most of the vacancies being produced at the end of range due to nuclear energy loss whereas in $Li^{3+}$ ion irradiation, most of the vacancies were created at the end of the region due to the dominance of electronic energy loss.
Figure 4.1  The TRIM results of the depth dependence of projected range ($R_p$) and the vacancy of (a) 120 keV Protons, (b) 50 MeV Li$^{3+}$ ions in Ti:LiNbO$_3$

Figures 4.2 and 4.3 shows the distribution of nuclear and electron energy loss as a function of penetration depth range for H$^+$ implantation and Li$^{3+}$ irradiation, respectively. For proton implantation, the target electron interacted with the proton ions and electronic energy loss takes place at near surface and continuously losing its energy. At the end of the region many thousands of collisions take place before ions come to rest due to target nuclei
and ion interaction which is called nuclear energy loss. In contrast to the situation with proton ion implantation, the incident swift energy Li³⁺ ions create location of electronic and nuclear damage peaks almost at the same position beneath the sample surface, i.e., at the end of ion’s trajectories. This means that the synergy of both effects should be taken into account for the structural and optical modifications in the damaged layer.

Figure 4.2  (a) Illustrative scheme of the generated buried amorphous layer (red strip) of nuclear damage. The blue strip indicates the region of electronic damage. (b) Plot of the electronic, $S_e$ (dashed lines), and nuclear, $S_n$ (solid lines), stopping power curves for 120 keV Protons, in Ti:LiNbO₃
Figure 4.3  (a) Schematic diagram of the generated buried amorphous layer (blue strip) near the maximum of the electronic damage. The red strip indicates the region of nuclear damage. (b) Distributions of electronic, $S_e$ (dashed lines), and nuclear, $S_n$ (solid lines), energy deposition of 50 MeV Li$^{3+}$ into Ti:LiNbO$_3$

4.4  STRUCTURAL ANALYSIS

HRXRD analysis was carried out for the samples using a Philips X’pert Pro materials research diffractometer (MRD) in the receiving slit operation mode with a single CuK$_\alpha$ line of wavelength $\lambda =1.54056$ Å and angular divergence of $\Delta \alpha =12$ arc sec. The Philips PW 3040 x-ray generator was operated at 40 kV and 10 mA. A four crystal Bartels type monochromator was employed using four Ge (220) reflections arrayed in the $(+,−,−,+)$ geometry (Bartels 1983). X rays generated from the monochromator were diffracted from (006) LiNbO$_3$ atomic planes with the $(+,−,−,+)$ geometry (Healey et al 1995). In order to record precise values of interplanar (d - space) distances, diffraction spectra of each samples were measured twice and the sample was rotated throughout. Interplanar spacings were calculated from the
expression \( d = \frac{\lambda}{2 \sin \left(\frac{\theta_A + \theta_B}{2}\right)} \), where \( \theta_A \) and \( \theta_B \) are the angular positions of maximum intensity in the diffraction spectra.

HRXRD spectrum (Figure 4.4a) with a well shaped, sharp spectrum and without any visible distortions was observed for the pure congruent LiNbO\(_3\) (CLNP) and reveals good structural quality of the wafer. HRXRD spectra recorded for the virgin, only implanted, only irradiated, and irradiation carried out on the implanted samples of 5 mol % titanium doped CLN are shown in Figure 4.4b-e. Diffraction peak for CLNP has full width at half maximum (FWHM) as 12.43 arc sec. It is nearly equal to angular divergence of Ge(220) monochromator of the instrument. Diffraction peak (Figure 4.4b) of titanium (5 mol %) doped congruent lithium niobate (CLNT5) indicates considerable broadening of (006) peak, i.e., 42.89 arc sec of FWHM because of lattice strain field (Hsu et al 1992, Avrahami and Zolotoyabko 1999) in the crystal introduced by the distribution of Ti ions. The presence of additional peak (\( \Delta \theta = +181 \) arc sec) with low intensity at the right side of the main peak may be due to lattice strain that appears to be uniform at deeper region.

HRXRD patterns recorded for the low energy (120 keV) proton implanted (fluence of \( 1 \times 10^{16} \) ions/cm\(^2\) ) sample (CLNT5) indicate different diffraction patterns for CLNT5 (Figure 4.4c). Two diffraction peaks were observed for implanted sample. The main peak was the narrow one having maximum intensity diffracted from the bulk samples. The satellite peak was from an implantation induced damaged layer. This satellite peak appears at higher angle side (\( \Delta \theta = +203 \) arc sec). The main peak in the diffraction pattern of the implanted sample exhibits the same shape as the virgin sample, which appears evidently due to the HRXRD from the bulk layer, i.e., confined between the \( H^+ \) ion depth range (0.8 \( \mu \)m) and the x-ray penetration depth (2 \( \mu \)m) (Avrahami and Zolotoyabko 1996). The additional diffraction peak is correlated to critical ion implantation induced defects and revealed inhomogeneous inflation of the crystal lattice. It reflects a higher magnitude of lattice strain due to interaction between ion beam and atoms in the target
material at the end of ion track (Destefanis et al 1979). HRXRD pattern recorded for high energy (50 MeV) Li\textsuperscript{3+} irradiated (1×10\textsuperscript{12} ions/cm\textsuperscript{2}) samples (CLNT5) indicates drastic reduction in their peak intensities. FWHM value was observed as 146.77 arc sec. The high energy swift ions produce heavily damaged layer up to the depth of 225 μm. HRXRD pattern recorded for the high energy (50 MeV) Li\textsuperscript{3+} irradiated (1×10\textsuperscript{12} ions/cm\textsuperscript{2}) on proton implanted samples, indicates marked improvement in the crystalline quality. FWHM was observed as 32.42 arc sec. Activation process (Bausa et al 1991) during irradiation (Li ions) drives the displaced atoms and recovers the damage partially for the original crystalline structure. This result reveals that the strain induced by ion implantation is much relaxed on Li ion irradiation.

![Graph showing diffraction spectra](image)

**Figure 4.4** High resolution x-ray diffraction spectra recorded for various LiNbO\textsubscript{3} samples: (a) CLNP; (b) CLNT5 virgin; (c) as implanted with 1 × 10\textsuperscript{16} H\textsuperscript{+} cm\textsuperscript{-2}; (d) as irradiated with 1 × 10\textsuperscript{12} Li\textsuperscript{3+} cm\textsuperscript{-2}; (e) both implanted and irradiated
It is well known that lithium, being small and mobile, can move from one medium to another medium by its thermal kinetic energy. Some loss of lithium from the implanted layers due to proton implantation was partially recovered by lithium ion irradiation. The use of lithium as an irradiation source has the advantages that this element is already a constituent of the crystal and no disturbing effects like formation of new compounds are expected. Irradiation of 50 MeV lithium ions on proton implanted lithium niobate samples create ion tracks in the samples and may lead to migration of weakly bonded (ionic character) lithium ions to the vicinity of the damaged surface in the LiNbO₃. The driving force for Li ions in the present sample is the buried positive charge which is built up in LiNbO₃ sample as a consequence of neutralization of the irradiated Li³⁺ ions when nearing the end of their track. At the end of irradiated ion tracks, there are no electrons available, the neutralizing electrons come from non-bridging oxygen atoms to which Li⁺ ions have weak ionic bond (Arnold and Borders 1977). This charge neutralization builds up a positive charge field and it acts as a driving force for Li⁺ ions towards the surface. Hence, the loss of lithium ions from the surface upon ion implantation may be partly compensated by the migration of lithium ions to the surface due to swift ion irradiation.

Conventional annealing process between 200 and 400 °C for several hours causes decomposition of hydrogen bond and considerable loss of protons from the waveguiding region. Also, it leads to creating tiny cavities or polymorphs (Nb₂O₅ or LiNb₃O₇) which give complexity to the crystal structure in the waveguiding path and is not favourable for guiding process (Lee et al 1986). Though, the temperature at the surface of the sample may not be exceeding 50 °C during irradiation (Bentini et al 2002), lithium ion irradiation on proton implanted samples improves the waveguide properties.
4.5 OPTICAL ANALYSIS

Optical transmission spectra on fine polished samples of CLNT5 were carried out with Varian Cary 5E UV-Visible-NIR spectrophotometer in the wavelength range of 200–800 nm. The incident unpolarized light beam from the spectrometer was propagated along the c axis on the Z-cut (001) samples. Figure 4.5 shows the optical transmittance spectra of CLNP, CLNT5 virgin, implanted, both implanted, and irradiated samples. The pure sample has transmittance of ~ 70% and cutoff wavelength at around 312 nm. Titanium doped (5 mol %) samples have transmittance of ~ 60%, slight yellowish in color and cutoff at 322 nm with redshift of 12 nm. The appearance of slight yellowish color of CLNT5 has been attributed to a small absorption “hump” in the visible region at 480 nm and, in turn, to charge transfer transition between the Ti$^{4+}$ or Ti$^{3+}$ (Bausa et al 1991) and the ligand oxygen.

Proton implantation on CLNT5 samples lead to a broad absorption in the range of 350 – 800 nm and drastic reduction in the transmittance. However, the absorption edge remains unchanged, even for the implanted (1×10$^{16}$ ions/cm$^2$) samples. A further decrease in optical transmittance was observed for the proton implanted samples on Li$^{3+}$ ion irradiation. The absorption hump becomes flattened on implantation or irradiation. The broad absorption (Schirmer et al 1991) (reduction in transmittance) in the samples has been attributed to several factors, (i.e) the change in refractive index patterns on implantation or irradiation, Li ion migration or activation, the formation of Ti$^{3+}$ ions, transition between the Ti$^{4+}$ or Ti$^{3+}$ and the ligand oxygen. The presence of the two valence (Ti$^{4+}$ or Ti$^{3+}$) states might lead to the existence of Ti$^{4+}$ – Ti$^{3+}$ pairs. The absorption band provides the measure of the number of Ti$^{4+}$ – Ti$^{3+}$ pairs in the medium.
Figure 4.5  Optical transmission spectra for the (a) CLNP; (b) CLNT5 virgin; (c) as implanted with $1 \times 10^{16}$ H$^+$ cm$^{-2}$; (d) both implanted and irradiated

4.6 SPECTROSCOPIC ANALYSIS

Hydrogen ion was always present in nearly all ABO$_3$ structures. It forms an OH$^-$ impurity complex and affects the properties and applications. The presence of OH$^-$ impurities play an important role in LiNbO$_3$:Fe holograms (Kovács et al 1991) and increase the spontaneous polarization and extraordinary index profile of the LiNbO$_3$ (Nahm and Park 2001). Hydrogen gets incorporated into the crystal from the humidity during crystal growth process in air (Bollmann and Stöhr 1977). The OH$^-$ stretching vibration was first observed by Smith et al (1968) and its detailed analysis was made by
Herrington et al (1973). The H\textsuperscript+ concentration and related structural information are deduced from IR absorption spectra. Fourier transform infrared (FTIR) and OH\textsuperscript− spectra were recorded for the pure CLN, CLNT5 virgin, implanted, and irradiated on implanted samples and are shown in Figures 4.6 and 4.7 respectively. Experiment was carried out in the 400–4000 cm\textsuperscript{−1} range using a Bio Rad FTS 40 spectrometer with resolution of about 1 cm\textsuperscript{−1}. IR absorption data were collected using unpolarized light transmitted parallel to the c axis of the crystal. The evolution of OH\textsuperscript− stretching band was observed in the infrared spectra of all the samples. Figure 4.7 (a) shows OH\textsuperscript− stretching band for CLNP. The spectra reveal a broad nonsymmetrical absorption of OH\textsuperscript− stretching band for CLNP with the peak at 3486 cm\textsuperscript{−1}. The FWHM of the band at 3486 cm\textsuperscript{−1} was 30.83 cm\textsuperscript{−1}. The broad spectrum was due to the presence of large number of vacancies and an incorrect sequence of Li and Nb cations. The shape of OH\textsuperscript− band around 3486 cm\textsuperscript{−1} (Bollmann and Stöhr 1977) is sensitive to the crystal composition, particularly the components of low energy (Kovács et al 1991) IR absorption spectra (Figure 4.7 (b)) of 5 mol % Ti doped CLN has peak at 3490 cm\textsuperscript{−1} a shift of around 5 cm\textsuperscript{−1} to the higher wavenumber. The absorption band changes from nonsymmetrical to fine structural and FWHM value decrease to 20.33 cm\textsuperscript{−1}. This indicates that more number of vacancies might be occupied by the Ti impurity ions and also rearrangement of Li and Nb cations to their position. Congruent crystals with less than 1 mol % dopants have no significant changes in their OH\textsuperscript− stretch modes. These results confirm that the transition metal ions (Mg, Ti, Cu, Cr, Fe) in lithium niobate practically do not support the incorporation of hydrogen in humidity (Schirmer et al 1991).
Figure 4.6 FTIR spectra of the specimen (a) CLNP; (b) CLNT5 virgin; (c) as implanted with $1 \times 10^{16} \text{ H}^+ \text{ cm}^{-2}$; (d) both implanted and irradiated
Figure 4.7  OH\(^-\) vibrational spectra of the specimen (a) CLNP; (b) CLNT5 virgin; (c) as implanted with \(1 \times 10^{16}\) H\(^+\) cm\(^{-2}\); (d) both implanted and irradiated.
Proton (H\(^+\)) implanted (fluence of \(1 \times 10^{16}\) ions/cm\(^2\)) CLNT5 sample shown in Figure 4.7 (c) has FWHM value as 21.20 cm\(^{-1}\), which is higher than that of CLNT5 virgin sample. The increase of FWHM in the proton implanted samples may be due to the relaxation of lattice (Yan et al 2004), because of the occupied protons. There is no prominent change in the OH\(^-\) absorption characteristics on Li\(^{3+}\) irradiation \((1 \times 10^{12}\) ions/cm\(^2\)) upon H\(^+\) implanted \((1 \times 10^{16}\) ions/cm\(^2\)) CLNT5 sample (Figure 4.7 (d)). The FWHM observed for the sample from the spectra was 21.12 cm\(^{-1}\). This slight variation in FWHM is due to thermal annealing with irradiation that causes outdiffusion of protons from the lattice and creates cation vacancies. Swift ion irradiation on H\(^+\) implanted sample does not alter the absorption band, however, modifies the crystal structure through rearrangement of interstitial and misplaced atoms.

4.7 SURFACE MICROSCOPE ANALYSIS

Atomic force microscope (AFM) is a powerful tool for true and three-dimensional imaging of surface down to subnanometer resolution without the need for any additional sample preparation such as ultrahigh vacuum, surface coating (Giessibl 2003), etc. AFM analysis was performed by a digital multimode SPM with Nanoscope IIIa controller in tapping mode over an area of 5×5 \(\mu\text{m}^2\) on pristine, implanted, irradiated, and irradiated on implanted samples (Figure 4.8). AFM image on the top surface of 5 mol % Ti doped CLN virgin substrate indicates smooth surface with roughness value of 1.52 nm (rms).
Blurred surface layer was observed for H\(^+\) ion implanted and Li\(^{3+}\) ion irradiated samples. The measured surface roughness (rms) values were 8.8 nm for implanted and 14.491 nm for Li\(^{3+}\) irradiated (CLNT5) samples. The rms roughness values of implanted and irradiated samples were nearly 6 and 10 times higher than that of virgin sample. The combined blisters observed on the surface of implanted and irradiated samples may be due to localized tilting of the lattice planes and the subsequent strain effect at near surface region. The surface roughness (4.799 nm) of Li\(^{3+}\) irradiated on H\(^+\) implanted CLNT5 sample was improved to smooth and flat type, which is visually observed from the image (Figure 4.8 (d)). The surface smoothness of this irradiated (on implanted) sample was improved by approximately two times to that of only implanted CLNT5 substrate. Implantation with lower energies creates an amorphous track (nanoscale) radius along their track (Olivares et al 2006) and may be responsible for surface roughness.

The flat view and section analysis of \((1 \times 10^{15} \text{ H}^+/ \text{cm}^2)\) implanted sample is shown in Figure 4.9. Implanted surface present hillocks surrounded by rims which are known as complex craters and simple craters were observed across \(1\times1 \ \mu\text{m}^2\). At higher fluences, i.e., \(1\times10^{16}\) and \(1\times10^{17}\) ions/cm\(^2\), restructured images with pits disappear. Average precipitate diameter of outer ring (indicated by green) around 148 nm with height around 0.66 nm was observed from the section analysis. Also, inner ring (indicated by red) had diameter around 48 nm and height around 1.62 nm. It is clearly evident that ion implantation offers an elegant way to produce nanometric radius ion precipitation.
Figure 4.8  3D and 2D AFM images of the different CLNT5 samples: (a) virgin; (b) as implanted with $1 \times 10^{16}$ H$^+$ cm$^{-2}$; (c) as irradiated with $1 \times 10^{12}$ Li$^{3+}$ cm$^{-2}$ and (d) both implanted and irradiated
Figure 4.8 (Continued)
Figure 4.9  AFM (a) flat view and (b) section analysis of CLNT5 sample implanted with $1 \times 10^{15}$ H$^+$ cm$^{-2}$ fluence
4.8 CONCLUSION

Low energy proton ion implantation and lithium swift ion irradiation were carried out on pure and doped congruent lithium niobate wafers. The relationship between the lattice strain produced by proton implantation and the formation of nanoscale restructured pits were demonstrated using HRXRD and AFM image measurements. Optical measurements reveal that the absorption edge remains unchanged after ion implantation and irradiation; however, the transmittance/absorbance was very much affected by the implantation as well as irradiation process. Titanium doping clearly suppresses the OH\(^{-}\) stretching vibration modes indicating the limited influence of humidity. Though proton implantation may enhance the intensity of the OH\(^{-}\) stretching vibration modes, Li ion irradiation activates the lattice and suppresses the intensity due to the outdiffusion of protons. AFM images indicate the presence of simple and complex craters with low fluence implantation on the surfaces. However, the defective pits were restructured with higher fluence of proton implantation as well as through activation by Li\(^{3+}\) ion irradiation on implanted samples. Formation of optical waveguide layer in titanium doped CLN through combination of buried layer of lithium as well as proton implantation was demonstrated.