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Structural and compositional characterization of $LiNbO_3$ crystals implanted with high energy iron ions

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ABSTRACT

Iron ions were implanted with a total fluence of 6×10^{17} ions/m^2 into lithium niobate crystals by way of a sequential implantation at different energies of 95, 100 and 105 MeV respectively through an energy retarder Fe foil to get a uniform Fe doping of about few microns from the surface. The implanted crystals were then annealed in air in the range 200–400 °C for different durations to promote the crystalline quality that was damaged by implantation. In order to understand the basic phenomena underlying the implantation process, compositional in-depth profiles obtained by the secondary ion mass spectrometry were correlated to the structural properties of the implanted region measured by the high resolution X-ray diffraction depending on the process parameters. The optimised preparation conditions are outlined in order to recover the crystalline quality, essential for integrated photorefractive applications.

1. Introduction

The exploding demand for high tech photonic devices for telecommunication, information technology, space and environment applications has led to a push for a greater integration and compactness. In this scenario, the combination of excellent electro-optical and non linear optical properties makes lithium niobate ($LiNbO_3$) an attractive host material for applications in integrated optics, especially in the field of holographic data storage. In particular, it is well known [1 and references therein] that iron – doped lithium niobate (Fe:LN) crystals present enhanced photorefractive response i.e. the refractive index can be suitably modulated by inhomogeneous illumination with light at visible wavelengths. In fact, photo-excitation of electrons occur from donor centres (mainly Fe^{2+}) into the conduction band. Provided that the illumination is inhomogeneous, those excited electrons redistribute and, consequently, are trapped in acceptor centres (mainly Fe^{3+} centres) by the interplay between diffusion, bulk photovoltaic effect and drift mechanisms. The electric field originated by this charge distribution induces a refractive index modulation by the electro-optic effect. In order to optimise the photorefractive response, the suitable iron concentration and the proper ratio between donor/acceptor centres should be used. As reported by [1], the photorefractive response is optimised when the Fe content is tuned in order to ensure the highest refractive index changes and the absorption from the iron doped matrix is kept at the minimum. Furthermore the best iron concentration lower than 2×10^{25} Fe/m^3 was suggested to achieve the above conditions. The photorefractive (PR) effects in Fe:$LiNbO_3$ with configuration of bulks as well waveguides have been investigated. In fact, the PR effects in Fe:LN waveguides strongly depend on the fabrication techniques. Some studies were presented on iron incorporation by the thermal diffusion [2,3] and few considered the Ti co-doping to guarantee the optical waveguiding conditions [4] The Ti in-diffused waveguides are with almost same of the bulks, and the proton exchanged waveguides usually lose the PR features considerably. For ion implanted waveguides, Tan et al. have shown that the PR properties are well preserved in the waveguides [5] and other works have also shown this indirectly [6,7].

In this work we report on the exploitation of high energy ion implantation in order to prepare locally iron doped regions on lithium niobate crystals. By ion implantation, in fact, controlled dopant concentration with a designed profile can be achieved by tailoring the ion beam irradiation parameters. Particularly in LiNbO3, waveguides can be produces by using ion beams. [8–12]. To our knowledge, iron implantation was never exploited in the past in this configuration. In this work Fe ions of 95, 100 and

Abbreviations: LN, lithium niobate; SIMS, secondary ion mass spectrometry; HR-XRD, high resolution X-ray diffraction.

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105 MeV were implanted through a 7.5 μm thick Fe foil at a fluence of 2×10^{17} ions/m^2 for each energy (total fluence: 6×10^{17} ions/m^2), to have a broader and uniform distribution of Fe in LN within the first 2 μm. SRIM computer code was used to simulate the thickness of degrader foil to get the broader distribution due to straggling. The compositional analysis of the implanted region was then carried out by exploiting the secondary ion mass spectrometry in order to check whether the in-depth distribution of the iron within the substrate was that expected by the design process parameters. Since the ion implantation process damages the crystalline structure, post annealing in dry air was carried out in order to recover crystal order. Different annealing conditions were systematically investigated (temperature ranging between 200 and 400 °C, annealing time from 30 min to several hours) by checking during the treatment the structural quality by the high resolution X-ray diffraction. The full recovery of the crystalline properties was thus followed evidencing the dynamics of the defects removal while the compositional analysis confirmed that the dopant still remains in the implanted region.

2. Material and experimental methods

Fe ions of 95, 100 and 105 MeV were sequentially implanted through a 7.5 μm thick Fe foil on commercial X-cut lithium niobate crystals (Crystal tech.) at a fluence of 2×10^{17} ions/m^2 for each energy (total fluence 6×10^{17} ions/m^2), to have a broad and uniform distribution of Fe in LN up to about few microns. The implantation was performed at the Inter-University Accelerator Centre, India using a ion beam current close to 1 pnA in vacuum conditions (10^{-6} torr in the irradiation chamber) and by scanning the beam by means of an electromagnetical scanning system. Post annealing treatments were carried out in dry air for temperatures ranging between 200 and 400 °C for durations starting from 30 min to several hours.

The implanted samples were then characterized by the compositional and structural point of views. In particular secondary ion mass spectrometry (SIMS) was exploited to measure the elemental in-depth profiles of chemical species in Fe implanted crystals. SIMS measurements were carried out by means of an IMS 4f mass spectrometer (Cameca, Padova, Italy) using a 14.5 keV Cs^+ primary beam and by negative secondary ion detection. The charge build up while profiling the insulating samples was compensated by an electron gun without any need to cover the surface with a metal film. The SIMS spectra were carried out at different primary beam intensities (50, 75 and 100 nA, stability better than 0.5%) rastering over a 150×150 μm^2 area and detecting secondary ions from a central region of the crater with an area close to 10×10 μm^2 to avoid border effects. The signals were detected in beam blanking mode (i.e. interrupting the sputtering process during magnet stabilization periods) in order to improve the in-depth resolution. The erosion speed was then evaluated by measuring the depth of the erosion crater at the end of each analysis by means of a Tencor Alpha Step profilometer with a maximum uncertainty of few nanometers.

The structural investigations were performed using a Philips MRD diffractometer with a sealed Cu anode source, equipped with a parabolic multilayer mirror for enhanced beam intensity. The beam was collimated and monochromatized using a four-bounce 2 2 0 channel – cut Ge monochromator giving a primary beam with a wavelength $\lambda = 0.154056$ nm, a spectral purity $\Delta\lambda/\lambda = 2 \times 10^5$ and an angular divergence of 0.0032°. The detector was a proportional counter equipped with a three bounce Ge 2 2 0 analyzer whose acceptance was equal to the divergence of the primary beam. In order to avoid artefacts due to thermal drifts during the measurements, the temperature of the measure chamber was stabilized at (25.0 ± 0.1) °C. The symmetrical 1 1 0, 2 2 0 and 3 3 0, and the asymmetrical 3 3 6 reflections were measured, by combining the standard rocking curves analysis with the reciprocal space mapping mode [13].

3. Results and discussion

In Fig. 1 we report the result of the SRIM2006 code [14] for the design of the implantation parameters, especially the stopping foil. The three iron profiles are shown depending on the implantation energy: the superposition of the three implantation energies is also indicated. Following the design parameters, an almost flat iron profile was expected in the range 500–1500 nm respectively. In Fig. 2, the result of the compositional analysis is shown: lithium, niobium, oxygen and iron SIMS signals (i.e. sputtering yield) are reported. In particular, the left axis refers to the iron concentration (the conversion between SIMS yield and Fe/m^3 was obtained using the nominal total implantation fluence). It is evident that a maximum Fe concentration close to 1.1×10^{23} Fe/m^3 was obtained in the doped region. Moreover, it is worth mentioning that the $LiNbO_3$ substrate appears to be affected by the sequential implantation: lithium and niobium and also oxygen, in fact, are not constant through the analyzed thickness. Although in the SIMS measure-

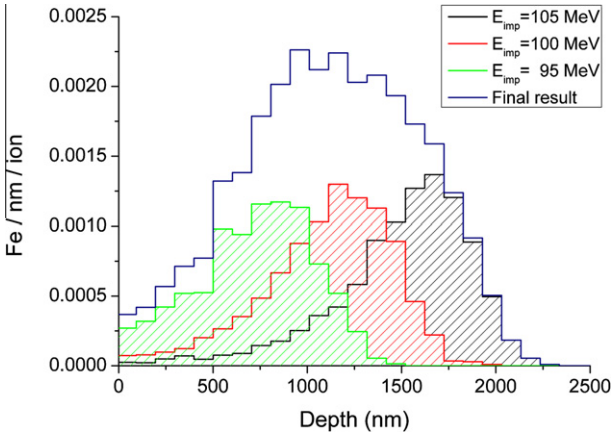

Fig. 1. Simulation of the iron in-depth distribution expected by the sequential implantations at 95, 105 and 110 MeV obtained by the SRIM code. The superposition of the three implantation energies is also indicated (final result).

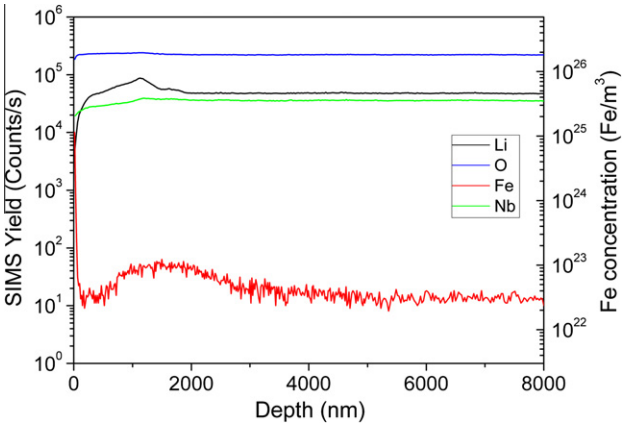

Fig. 2. As implanted sample: lithium, niobium, oxygen and iron in-depth profiles measured by the SIMS technique. The minimum detection limit of the SIMS technique in the present case is close to 2×10^{22} at/m^3, while the mass interference effect due to the presence of contributes to the mass 56 which is not due ^{56}Fe (such as $(^6Li_2{}^{16}O)_2$) gives a background of the order of 10 counts/s.