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Morphology of ion tracks and nanopores in $LiNbO_3$ produced by swift-ion-beam irradiation

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Abstract

The surface of $LiNbO_3$ crystals after swift ion irradiation in the low velocity regime has been investigated by optical and atomic force microscopy (AFM). Samples were irradiated with Cu 50 MeV, Cl 46 MeV and Br 12 MeV ions. Before any additional treatment the surface of the sample irradiated with Cu ions shows hillocks of a 5–8 nm diameter and of 5 nm in height. The latent tracks were subsequently etched at room temperature with $HF:HNO_3$ solutions during a few minutes. The shape of the surface pore caused by etching was strongly anisotropic for the Cu irradiations and only slightly anisotropic for the Br irradiations. The larger track length and surface stopping power for the Cu 50 MeV ions is most likely the origin of the final difference in pore shape via the induced swelling and enhanced etching rate. Optical waveguide measurements were also performed in the case of Cl irradiations to obtain in-depth averaged values of internal amorphization and track radius.

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1. Introduction

Swift ions create, in many materials, amorphous tracks along the ion trajectories [1–3] whenever the electronic stopping power S_e is above a certain threshold value S_{th}. These tracks, appearing as tiny hillocks on the surface, have diameters of a few nanometers depending on irradiation conditions (ion and energy) [4,5]. The mechanisms responsible for track formation rely on electronic excitations and the subsequent energy transfer to the ionic lattice to produce damage and amorphization. Different calculations based on a thermal spike approach have been developed to account for track formation as well as to predict the nanometric track radius [6,7]. The morphology and depth profile of the tracks is a relevant information to test theoretical models. On the other hand, the tracks can be selectively etched [3] to produce (surface) pores and nano-channels that, in turn, can be refilled with inorganic or organic substances. A number of applications of the ion-track technology has been proposed and/or tested, going from fission-fragment dosimetry, to molecular sieves, and to a variety of electronic and magnetic devices [5,8–10].

$LiNbO_3$ is a reference material for the development of photonic applications and electrooptic and nonlinear optical devices. The use of swift ions has started to be explored for such applications [11]. For the current and potential new applications based on the ion-track technology a detailed study of the ion tracks is crucial. The main purpose of this work was to learn about the morphology

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(topography changes and depth profile) of the tracks generated in $LiNbO_3$, before and after an etching treatment, particularly working with ions of specific energy around or below about 1 MeV/amu. To our knowledge no systematic investigation of this topic is available in the literature, although a few data have been reported [4,12].

2. Experimental

Congruent $LiNbO_3$ single crystal optical grade polished plates purchased from Casix were irradiated with Cu, Br and Cl ions in the 5 MV tandem accelerator [13] recently installed at the Center for Microanalysis of Materials (CMAM) at the University Autónoma of Madrid. The irradiation parameters are shown in Table 1. The stopping powers at the surface are, respectively, 12, 6 and 7 keV/nm, i.e. above the threshold value around 5 keV/nm determined for $LiNbO_3$ by independent methods [14,15]. Total irradiation fluences were in the range 10^9–10^{11}cm^{-2} for surface topography measurements by AFM (atomic force microscopy) and 10^{11}–10^{13}cm^{-2} for optical characterization (i.e. refractive index measurements). Chemical etching was performed at room-temperature using a mixture solution (1:1) of HF (40% vol.) and HNO_3 (70% vol.) for a variable time ranging from 30 s to 30 min. Surface topography before and after chemical etching was measured with an air AFM microscope with a tip size of about 10 nm.

For Cu and Br ions the stopping power decreases with depth whereas it reaches a maximum inside the crystal for Cl 46 MeV ions. Then, for Cl irradiations, the (amorphous) track diameter should increase with depth from the surface to the maximum of S_e generating a gradual decrease of the refractive index which allows for optical waveguiding at the surface. Therefore, by application of the standard prism-coupling dark mode technique the refractive index depth profile can be determined [16]. By using a simple averaging approach, and knowing the amorphous refractive index value of $n = 2.10$ (at $\lambda = 633$ nm) [11,15], the amorphized areal fraction and thus the radius of the individual tracks as a function of depth can be obtained. The depth limit of the method corresponds with the minimum of the refractive index profiles and to the maximum track diameter, being at about 4 μm. As a complementary check RBS/channeling experiments using He ions at 5 MeV were also performed. By comparing the random and channeled spectra the data provide the surface fraction that has been heavily damaged during irradiation.

Table 1
Irradiation parameters of the $LiNbO_3$ samples investigated

Ion	Energy (MeV)	MeV/amu	S_e (keV/nm)	R_p (μm)
^{63}Cu	50	0.8	12	7.2
^{35}Cl	45.8	1.3	6.8	8.1
^{79}Br	12	0.15	6.1	3.3

S_e is the electronic stopping power at the surface; R_p is the projected ion range.

3. Results on irradiated unetched samples

3.1. Surface topography

After irradiation with Cu ions of 50 MeV, the surface topography has been inspected with AFM microscopy on a *z*-cut sample. Fig. 1(a) shows a 3D view of the surface topography. Hillocks with nearly circular cross sections of 6–8 nm diameter and of 5 nm height are observed on the surface, taking into account the convolution with the AFM tip size. On the other hand the radius of the tracks at the surface derived from RBS/channeling yields gives a similar value (see Fig. 2(b)).

3.2. Depth profile of the tracks

In order to determine the track radius as a function of depth, refractive index measurements were performed on samples irradiated with 46 MeV Cl ions. Fig. 2(a) illustrates the refractive index profiles obtained for three fluences, and Fig. 2(b) shows the variation of the track

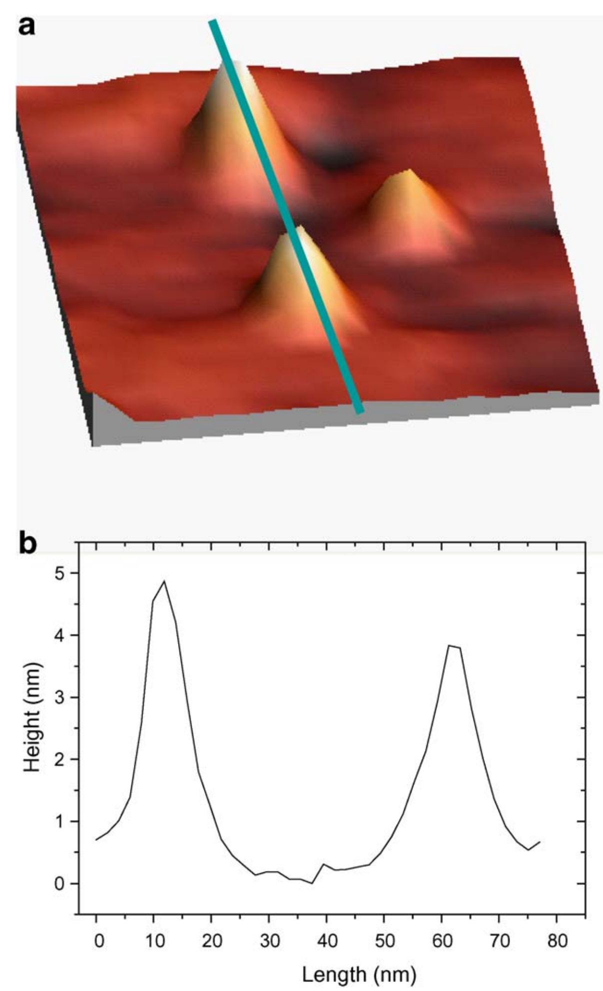

Fig. 1. AFM 3D image of a $LiNbO_3$ surface showing hillocks induced by Cu ion irradiation at 50 MeV; the height profile along the line is also shown below the image.