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## Morphological and Electrical studies of Lithium Ion Implanted Sodium Potassium Niobate Single Crystal grown by Flux Method

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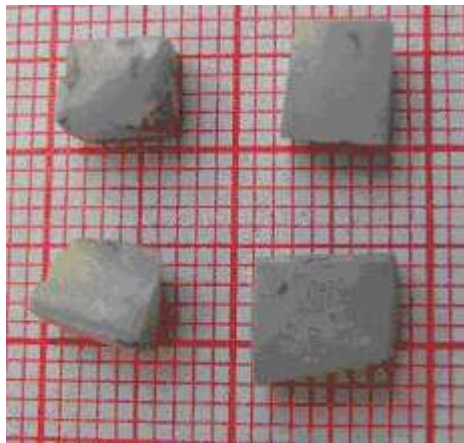
**Abstract:** Sodium potassium Niobate (KNN) single crystals were subjected to <sup>7</sup>Li ion (100 keV) implantation with different fluences ( $10^{15}$ ,  $5 \times 10^{15}$  and  $10^{16}$  ions/cm<sup>2</sup>) at normal and oblique angle of incidences. Evolution of Li ion impact on surface and structural properties of KNN sample have been ascertained by AFM and XRD spectra. The decrease in crystallinity of KNN single crystals on <sup>7</sup>Li ion implantation and SEM analysis show dramatic changes in the surface observed. AFM observation shows that the normal angle incidence creates more number of defects in the implanted region whereas oblique angle incidence ( $\theta=30^\circ$ ) creates strain layer closer to the surface and roughness values increase after irradiation.

**Keywords-** KNN; SEM; AFM; Raman.

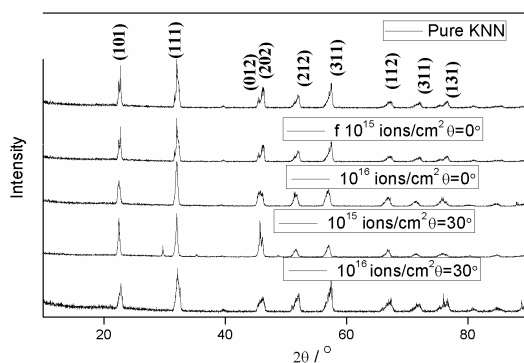
### Introduction and Experimental

Sodium potassium niobate single crystal have shown a piezoelectric coefficient of  $d_{33} \sim 110\text{pC/N}$  and a Curie temperature of  $T_c \sim 400^\circ\text{C}$ . These values are comparable with the conventional PZT materials [1,2]. Ion-beam irradiation and implantation with suitable energies provides a unique and exciting way of modifying and controlling the surface properties of a solid over a precisely defined skin depth, adding a defined concentration of impurities on the surface region. This enables to engineer the material properties such as controlling the crystallinity, which is much superior to other methods of surface modification [3]. Low energy ion bombardment can also be used for a variety of thin film applications such as ion beam etching and patterning of surfaces and assisting deposition and growth of thin films on suitable substrates. Ion implantation on surfaces at an oblique incident angle produces surface modifications with variety of features than normal incidence. This

can be utilized to get nano patterned surface features, quasi periodic ripples or wavy features on surface and optical grating. In the present chapter discuss the modification of surface morphology produced by low energy 100 keV Li ion implantation as a function of fluencies at various incident angles with respect to the surface normal in KNN single crystal surfaces. Good quality KNN single crystals with polished surface were used after cleaning with ultrasonically and acetone to remove the residual polishing surface damage as shown in the Figure 1. The dimensions of KNN samples are  $\sim 5 \times 5 \text{ mm}^2$  with thickness of  $\sim 0.8 \text{ mm}$ . The samples were implanted at normal and oblique ( $\theta=30^\circ$  and  $60^\circ$ ) angle with  $^7\text{Li}$  ion beam delivered at 100 keV by the linear accelerator at Inter University Accelerator Centre, New Delhi, India. All implantations were performed at room temperature. The vacuum in the radiation chamber during the experiment was about  $8 \times 10^{-7}$  mbar. Lithium of energy 100 keV and the ion fluencies were selected as  $10^{15}$ ,  $5 \times 10^{15}$  and  $10^{16}$  ions/cm<sup>2</sup>. To avoid charge pileup, the beam current was maintained as  $\sim 10 \text{ nA}$  for implantation and  $0.5 \text{ nA}$  for irradiation processes.



**Figure 1** :Photographs of obtained KNN single crystals grown using KF-NaF flux.



**Figure 2** : Powder X-ray diffraction pattern of unimplanted and 100 keV Li ion irradiated with different angle of implanted KNN single crystals

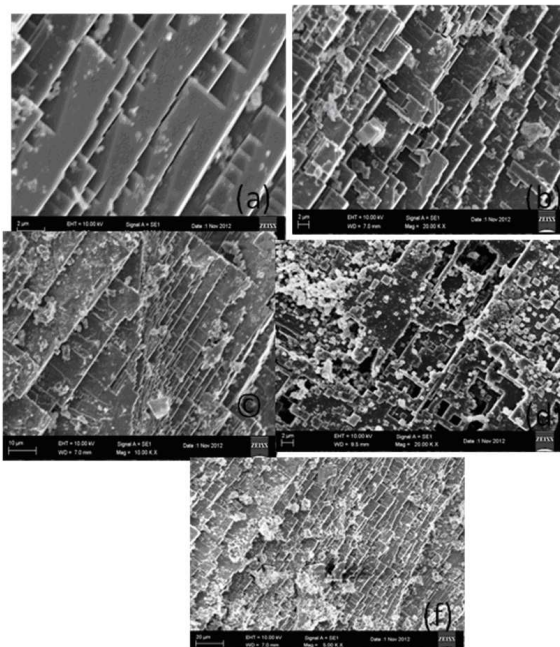
## Results and Discussion

Figure 2 show the XRD spectra of Li ions (100 keV) implanted samples. After ion implantation, the lattices have a high degree of disorder due to nuclear collisions between the implanted ions and target ions and between recoil-recoil the knock-one of the host ions. XRD spectra taken for  $10^{16}$  ions/cm<sup>2</sup> implanted at two different angle ( $\theta= 0^\circ$  and  $30^\circ$ ) are compared. The obtained curve show that the damaged peaks are located at higher angle side and normal angle ion implantation more number of extended structures can be seen. Implantation of  $\theta= 30^\circ$  incident angle shows the additional peaks are located at right side near to the main diffraction peak. Also splitting of the extended structure can be observed. From the above observations, the normal angle incident creates more number of defects in the implanted region where the oblique angle incident  $\theta= 30^\circ$  created strained layer near the surface. These spectral features originate due to the implantation damaged layer, which has reduced lattice parameter than the undamaged region. The implantation induced lattice contraction relates to the formation of pairs of Frenkel defects consisting of both interstitial and vacancy. The extended peak in the ion implanted layer were due to the local insertion of Li interstitials that causes a

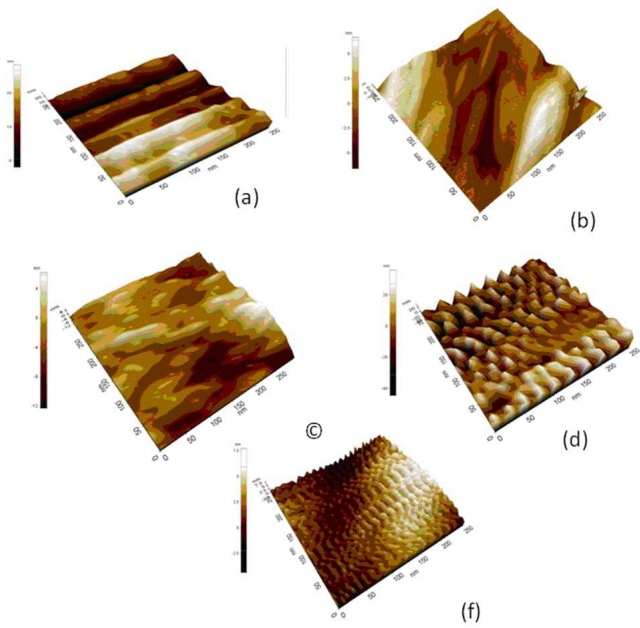
compressive strain the lattice region parallel to the surface. Surface evolution of Li ion implantation induced defects of KNN crystals were studied by using JEOL T-330 scanning electron microscope (SEM).

Figure 3 shows a series of SEM images of KNN surfaces implanted by 100 keV Li ions at various angles of incident for  $10^{16}$  ions/cm<sup>2</sup>. SEM investigation reveals drastic modifications on the surface morphology and distribution of crystalline imperfections induced by energetic ion. It is clearly seen that unimplanted sample has no visible surface modification whereas implanted contain combined blisters and protrusion like surface morphology. At normal angle incident nearly circular type surface defects are observed. Varying the incident angle to off normal ( $\theta=0^\circ$  and  $30^\circ$ ), more varied surface features are observed. The observed images for  $\theta=30^\circ$ , show circular type defects with elongated defects

Typical AFM image of the surface of KNN implanted with Li ions(100 keV) with fluencies of  $10^{15}$  and  $10^{16}$  ions/cm<sup>2</sup> at  $\theta=0^\circ$  and  $30^\circ$  incident angle are shown in Figure 4. Atomic force microscope analysis was performed by digital Nanoscope IIIa controller in tapping mode over an area of  $1 \times 1 \mu\text{m}^2$  on pristine, normal and oblique angle incident samples. The dome like protrusions with amorphous layer observed on various fluence at normal angle incidence. The irregular dome like protrusions can be seen for  $10^{15}$  ions/cm<sup>2</sup>, where large size protrusions were observed with a fluence of  $10^{16}$  ions/cm<sup>2</sup>. The protrusions are identified as bright images with a distorted surface structure in hemispherical shape of the KNN surface in AFM image. The measured r.m.s surface roughness for  $10^{15}$  and  $10^{16}$  ions/cm<sup>2</sup> are 8.01 and 10.73 nm respectively. Varied surface features of elongated protrusions are observed for incident angle of  $\theta=30^\circ$ . Blisters with raised regions elongated in the ion incident angle direction are observed for  $10^{15}$  ions/cm<sup>2</sup>. When increasing the fluence to one order of magnitude, the surface structures show clearly that blisters has an irregular shape with a disturbed lateral atomic arrangement of the surface. 3D AFM images of  $10^{15}$  ions/cm<sup>2</sup> clearly indicate that the bright spot which corresponds to blisters and dark contrast spot correspond to the surface vacancy defects, the dark contrast spot appears probably due to the strain of the crystal around the amorphous region. Hence it is concluded that the dome like protrusion and blister along with small hillocks were produced at the ion-impacted region due to the pushing effect towards the surface and thermalization process with vacancy formation the surface during the Li ion implantation at various angles of incident.



**Figure 3:** SEM images of surface features of unimplanted (a) and implanted with 100 keV Li ion with fluency (b)  $10^{15}$  ions/cm<sup>2</sup> and (c)  $10^{16}$  ions/cm<sup>2</sup> at angle  $\theta=0^\circ$  (d)  $10^{15}$  ions/cm<sup>2</sup> (e)  $10^{16}$  ions/cm<sup>2</sup> at angle  $\theta=30^\circ$ .



**Figure 4:** 3D AFM images of surface features of unimplanted (a) and implanted with 100 keV Li ion with fluency (b) $10^{15}$  ions/cm<sup>2</sup> and (c)  $10^{16}$  ions/cm<sup>2</sup> at angle  $\theta=0^\circ$ (d) $10^{15}$  ions/cm<sup>2</sup> (e)  $10^{16}$  ions/cm<sup>2</sup> at angle  $\theta=30^\circ$

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