Materials Research Express

PAPER

Investigation of structural and morphological properties of high energy ion irradiated KNN films

Radhe Shyam1, Deepak Negi1, Apurba Das2, Pamu Dobbidi* and Srinivasa Rao Nelamarri1,*

1 Department of Physics, Malaviya National Institute of Technology Jaipur, J.L.N. Marg, Jaipur 302017, India
2 Department of Physics, Indian Institute of Technology Guwahati, Guwahati 781039, India
* Author to whom any correspondence should be addressed.
E-mail: srnelamarri.phy@mnit.ac.in

Keywords: KNN thin films, ion irradiation, crystal structure, morphology, power spectral density

Abstract
The transfer of high localized energy density to target matrix via swift heavy ion provides a domain to engineer the properties of materials in a systematic and controlled mode. The present study describes the influence of ion irradiation on structural properties and surface morphology of (K,Na)NbO3 (KNN) films of thickness 650–750 nm irradiated with 100 MeV Ni ions at different fluences varying from $1 \times 10^{12}$ to $1 \times 10^{13}$ ions cm$^{-2}$. Multiple ion impact induced reduction in crystalline behavior of KNN perovskite is observed as an effect of ion fluence. The films show partially amorphized nature with ion fluence, and are remained in crystalline perovskite phase after irradiation with decreased peak intensities. Quantitative surface roughness and surface scaling study via power spectral density (PSD) analysis were carried out using atomic force microscopy (AFM) micrographs. The root mean square roughness decreased at $1 \times 10^{12}$ ions cm$^{-2}$ and thereafter, increased monotonously with increasing ion fluence. The adatoms mobility and coalescence effect might have caused the variation in roughness. From the PSD results, modification of surface morphology of films irradiated at $1 \times 10^{12}$ ions cm$^{-2}$ is attributed to the competing mechanisms of viscous flow and evaporation-recondensation processes. At higher fluence, the evolution mechanism of morphology is turned out to be the combined effect of evaporation-recondensation and diffusion processes. The microstructures obtained using scanning electron microscopy are correlated with the AFM results. The dominating processes of irradiation induced modification in the morphology of KNN films are studied in detail, and this study will be useful from both fundamental and applied perspectives.

1. Introduction

The advancement of a new category of lead-free ceramics has become a broad research area for scientists and engineers. Potassium sodium niobate ((K,Na)NbO3) (KNN) is one of the most potential candidates among various lead-free materials owing to its admirable piezoelectric properties with Curie temperature of above 400 °C [1]. The lead-based piezoelectric ceramic material such as Pb(Zr, Ti)O3 contains more than 60 wt.% lead, which is detrimental for the environment [1, 2]. Such limitations have led to ever growing demands for lead-free ceramic-based products day by day. KNN-based thin films have found prominent use in diverse applications such as energy harvesters, microelectromechanical system, and optical devices [3–5]. Numerous techniques have been adopted for the deposition of KNN thin films that include chemical deposition [6], sol-gel [7], RF magnetron sputtering [3, 4], pulsed laser deposition [8], etc. Among these techniques, RF magnetron sputtering is a potential tool for the deposition of high quality, dense, and uniform thin films with a large deposition area. Recently, tailoring growth modes by excess alkali addition in sputtered KNN thin films has been reported [9]. A few studies have already been implemented to improve the properties of KNN thin films such as doping, annealing, varying sputtering parameters, deposition methods, etc. In addition to these methods, ion-matter interaction is also a potential approach to tune the properties of materials in a controlled manner. The ion beam facility has offered a new possibility of synthesis, and modification of materials at nanoscale [10]. Therefore, a
study dealing with the interaction of ion beam with KNN thin films for tuning its properties is of utmost importance. The study of swift heavy ion (SHI) irradiation has been established as a promising method for tuning the properties of nanostructured materials. SHI irradiation study has become a versatile technique which can engineer the properties of target materials in the controlled and selective way based on the energy, mass, and fluence of incident ion [11, 12]. The formation mechanism of surface features of few nanometer sizes with impact of SHI and slow highly charged ions is discussed in a review report [13]. In the recent study, the improvement in piezoelectric properties of triglycine sulphate single crystal irradiated using 100 MeV Ni ion beam is reported [14]. It is explained that SHI irradiation can enhance the piezoelectric properties of materials probably due to induced defects density. It may create dangling bonds at the surface that lead to the local deformation of crystal structure. Further on applying the electric field in a particular direction on sample, it may increase the magnitude of deformation.

Furthermore, several reports can be found in literature that explain the irradiation induced modification in surface roughness and surface smoothening behavior for different materials [15, 16]. The competing mechanism between roughening of the surface due to irradiation induced sputtering, and surface smoothening as a consequence of adatoms’ motion by surface diffusion causes the evolution of surface features during ion beam irradiation. Saravanan et al [17] reported the effects of irradiation using a 45 MeV Li ion beam on structural and morphological properties of KNN single crystal synthesized by flux method. In the previous study, the modifications in structural and optical properties as an effect of ion beam irradiation on KNN films prepared by RF magnetron sputtering in pure Ar as well as the mixed environment of Ar and O₂ have been investigated [18, 19]. However, there is no systematic study on the evolution of surface features of KNN thin films using surface scaling theory within the purview of the existing model. The properties of films deposited using sputtering are highly dependent on the morphology of thin films. It is essential to understand the factors affecting the surface morphology and its fundamental mechanism because roughness of thin films plays a crucial role in the performance of devices [20]. The smooth surface is required for most of the technological applications in electronic and optical devices because these technologies are hindered by inherent surface roughness by an escalation of separate islands during growth process. Furthermore, the dependency of decay lifetime on surface defects/ grain boundaries is observed in our recent study on light-emitting defects in KNN thin films as an effect of ion irradiation [21]. This motivates us to investigate further SHI irradiation induced study on surface evolution and kinetics of KNN films prepared by RF magnetron sputtering.

The present work is mainly focused on the effect of SHI irradiation induced structural and surface modification of KNN films, which were deposited in pure Ar ambience using RF magnetron sputtering. Films were irradiated at different fluences varying from 1 × 10¹² to 1 × 10¹³ ions cm⁻² with 100 MeV Ni ions. After SHI irradiation, power spectral density (PSD) analysis from atomic force microscopy (AFM) micrographs was carried out to comprehend the smoothening mechanism of films. The structural and morphological studies of pristine and ion beam irradiated KNN films were studied using X-ray diffraction (XRD), AFM, and field emission scanning electron microscopy (FESEM).

2. Experiment

The conventional solid-state reaction process was adopted for synthesizing the KNN sputtering target by taking high purity powders of Na₂CO₃, K₂CO₃ and Nb₂O₅ (Sigma Aldrich, USA). The detailed procedure of target preparation has been published elsewhere [5]. KNN films were deposited at room temperature on Si substrates using RF magnetron sputtering (Advanced Process Technology, India). The deposition of KNN films was done at ~2.6 × 10⁻² Torr pressure at 20 SCCM argon gas by maintaining a fixed sputtering power of 40 W. Substrates holder was mounted above at a gap of ~5 cm from sputtering target, and during deposition, it was rotated consistently for the uniform deposition of films. The thickness of RF-sputtered KNN films is in the range of 650–750 nm. Afterward, to obtain crystalline KNN films (pristine films); as-deposited samples were annealed in air ambiance at a temperature of 700 °C for an hour. Ultimately, the annealed films were subjected to SHI irradiation with 100 MeV Ni ions using the 15UD Pelletron Accelerator facility situated at Inter-University Accelerator Centre (IUAC), New Delhi, India. Ion irradiation of KNN samples was done at various fluences varying from 1 × 10¹² to 1 × 10¹³ ions cm⁻². Figure 1(a) represents the schematic illustration of ion beam interaction with matter. The electronic energy loss (Sₚ, transferred to target electrons) of 100 MeV Ni ions in the KNN matrix is 1.15 keV Å⁻¹, whereas nuclear energy loss (Sₙ) is 2.23 eV Å⁻¹, estimated using SRIM-2013 simulation program as shown in figure 1(b). Therefore, Sₚ plays an imperative character in the modification of properties of KNN films in present study. The projected range of Ni ions, which go deep inside the substrate, into KNN is 12.41 μm and, therefore, neglects the possibility of Ni ions getting embedded in the KNN matrix.

The crystalline phase analysis of pristine and SHI irradiated KNN samples is carried out using Cu-Kα (1.54 Å) monochromatic X-rays. The surface topography of pristine and irradiated films is analyzed using an
atomic force microscope (Bruker, MultiMode 8, Germany). The 2D isotropic PSD data was taken out from AFM images in order to identify the evolution mechanism of surface features before and after ion beam irradiation. A field emission scanning electron microscope (FESEM; FEI Nova NanoSEM 450) was utilized to study surface morphology and grain size estimation.

3. Results and discussion

Figure 2 depicts the X-ray diffraction (XRD) pattern of pristine and irradiated films at different ion fluences. It is evident from the XRD spectra that pristine KNN film has a typical pseudocubic crystalline phase of perovskite structure with (001)-preferred orientation. Pristine KNN film exhibits polycrystalline nature with various crystal planes of (001), (110), (002), and (112) situated at 22.63°, 32.17°, 46.17°, 51.81°, and 57.26°, respectively. The induced effect of ion irradiation with different fluences on XRD spectra can be observed from figure 2. It is seen that the peak intensities of various crystal planes are decreased monotonously upon irradiation with increasing ion fluence. The decrease in the crystalline peak intensities of KNN perovskite with an increase in fluence is probably due to the overlapping of fluence, which creates defects in crystal lattice resulting in the partially amorphized behavior of films [18]. Since the electronic energy loss is very high compared to nuclear energy loss (shown in figure 1(b)), most of the incident Ni ion beam energy is transferred to electrons of the target atoms via electronic energy loss. According to thermal spike model, the incident energy is distributed...
between electrons via electron-electron coupling, and subsequently, is transferred to the lattice by electron-phonon interaction [22]. Therefore, an enormous amount of energy is transferred to the target atoms along the path of projectile and accounts for the formation of zones of high temperature in the surroundings of ion path. Due to temperature spike, the pressure waves might have generated that may lead to the structural order/ disordering and strain in the crystal structure and thus, affecting the peak intensity of KNN upon ion irradiation [23]. Moreover, the intensity ratio corresponding to more preferential (001) and (110) planes of pristine and irradiated films is calculated in order to estimate the degree of preferred orientation of KNN perovskite and is observed to be 2.7 for pristine films, as shown in table 1. The obtained value indicates that the grains are preferentially more orientated along [001]. This intensity ratio is found to increase after irradiation, and the values for irradiated films are observed in the range of 3.0–3.9, as given in table 1.

Moreover, the average crystallite size ($D$) of pristine and irradiated samples is estimated using Scherrer’s formula [24] given as: 
$$D = \frac{0.9\lambda}{\beta \cos \theta_B},$$
where $\beta$ is full width at half maximum in radians, $\lambda$ denotes the wavelength of Cu-K$_\alpha$, X-ray (1.54 Å), and $\theta_B$ represents Bragg diffraction angle. The average crystallite size of KNN was determined from the most intense (001) peak in XRD spectra. The average crystallite size of the pristine sample is $\sim$18.5 nm, while it is found to be decreased after ion beam irradiation, as tabulated in table 1. Reduction in the crystallite size from 18.5 nm (pristine sample) to 16.0 nm (irradiated films at fluence $1 \times 10^{12}$ ions cm$^{-2}$) could be attributed to the structural disintegration of materials resulting from numerous ion impacts by SHI irradiation [25]. Further, a minor and non-monotonic improvement in the crystallite size is observed with ion fluences. The reduction in crystallite size after irradiation can be explained based on the amorphization of material with ion fluences, as discussed above. The considerable energy imparted to the target system leads to increase in the local temperature surrounding the path of projectile that may cause the breaking of crystallites. These crystallites may be rejoined upon multiple ion impact, which consequences the slight increase in crystallite size upon increasing fluence. Therefore, the increase in crystallite size at $5 \times 10^{12}$ ions cm$^{-2}$ can be ascribed to the aggregation of these fragmented crystallites. The similar behavior of an increase in crystallite size at higher fluence has been reported in literature [16, 26]. This aggregation after irradiation is further correlated with AFM results, as discussed in the next section. Moreover, it is identified that the crystalline peaks of KNN have shifted slightly towards lower angle, as shown in figure 3. This might be due to some strain relaxation as a result of SHI irradiation. Besides the shifting of peaks, it is also clearly seen from XRD spectra (represented in figure 4) that (012) crystalline peak of KNN is split into doublet more efficiently after irradiation. The relative intensity of these peaks is affected by irradiation at different fluences. The similar kind of outcomes has been observed previously for composite KNN ceramic [27]. The tendency of domain switching (increase in the intensity of shorter peak relative to other peak in doublet) indicates the co-existence of phases in KNN system caused by SHI irradiation. These results suggest that ion beam irradiation induced a structural order-disorder in KNN system that may lead to crystalline phase transition in KNN perovskite. Furthermore, films also show a significant amount of secondary phases ($K_2Nb_6O_{16}$) along with the KNN crystalline phase. The formation of this phase might be due to high volatilization rate of alkali species, and it forms at a lower temperature than that of KNN phase. Similar behavior for the formation of pyrochlore phases in various forms has been reported by different authors [28–30]. The weight percentage of $K_2Nb_6O_{16}$ in the films is quantified from the following relation [31]:

$$W_A = \frac{1}{1 + 1.265 \left(\frac{I_A}{I_B}\right)} \times 100\quad (1)$$

where $W_A$ denotes the weight percent of $K_2Nb_6O_{16}$, $I_A$ and $I_B$ are the intensities of most intense peak of secondary phase and KNN perovskite, respectively. The obtained value of weight percent of the secondary phase for pristine and ion beam irradiated samples was converted into atomic percentage, and the values are listed in table 1. The amount of $K_2Nb_6O_{16}$ phase is found to be decreased to minimum value (1.2) for films irradiated at fluence $1 \times 10^{12}$ ions cm$^{-2}$. The characteristic of variation in amount of secondary phase is quite similar to the average crystallite size of KNN with ion fluence. Therefore, the energy transferred to the material via electronic

| Samples | Average crystallite size (nm) | $I_{001}/I_{110}$ | Atomic percentage of secondary phase |
|---------|------------------------------|-------------------|-----------------------------------|
| Pristine | 18.5 ± 0.1                   | 2.7               | 2.9                               |
| $1 \times 10^{12}$ ions cm$^{-2}$ | 16.0 ± 0.1               | 3.9               | 1.2                               |
| $5 \times 10^{12}$ ions cm$^{-2}$ | 16.8 ± 0.1               | 3.1               | 3.1                               |
| $1 \times 10^{13}$ ions cm$^{-2}$ | 16.1 ± 0.2               | 3.0               | 2.2                               |
excitation, and ionization of target atoms is responsible for the partial amorphized zone along the path of ions, which might have caused the modification of structural properties of KNN perovskite.

Before and after Ni ion irradiation, the surface topography of KNN samples is studied using AFM. Figure 5 depicts the 3-dimensional AFM images of pristine and irradiated KNN samples with a scan area of $3 \times 3 \, \mu m^2$. The root mean square roughness ($R_{\text{rms}}$) of these KNN films is evaluated using the expression [32]: $R_{\text{RMS}} = (\langle h^2(r) \rangle - \langle h(r) \rangle^2)^{1/2}$; where $h(r)$ represents the height of surface features at a position $r = (x, y)$.

The obtained $R_{\text{rms}}$ value for a pristine sample is $\sim 10.6$ nm, whereas, for irradiated films at fluence $1 \times 10^{12}$, $5 \times 10^{12}$ and $1 \times 10^{13}$ ions cm$^{-2}$, is found to be around $\sim 4.9$, $\sim 8.3$ and $\sim 8.8$ nm, respectively (shown in

![Figure 3. XRD peak shifting of (001) plane and (012)/(210) plane (inset) after ion beam irradiation.](image)

![Figure 4. XRD spectra of Gaussian fitted (012) and (210) planes before and after irradiation.](image)
The variation in surface roughness shows the significant consequences of ion beam irradiation on the surface topography of KNN films. During the passage of energetic ions through the material, the transferred energy leads to enhancing the mobility and rearrangement of surface atoms of target material and can be accountable for the surface morphology modification [33] of KNN thin films. The $R_{\text{rms}}$ of KNN films is observed to decrease from 10.6 nm to 4.9 nm upon irradiation at $1 \times 10^{12}$ ions cm$^{-2}$. However, the roughness of films is slightly increased monotonically after irradiation beyond the initial fluence. The sharp decrease in surface roughness of films irradiated at fluence of $1 \times 10^{12}$ ions cm$^{-2}$ shows the smoothening of surface occurring at an initial fluence. The smoothening can be due to viscous flow, evaporation and recondensation, volume, or surface diffusion, which takes place on the surface of films after the impact of ion irradiation. Furthermore, it is found that the average lateral size and height of surface features of AFM images also decreased upon irradiation at $1 \times 10^{12}$ ions cm$^{-2}$, as listed in table 2. Log-normal fitted size distribution of surface features of films before and after irradiation at different ion fluences is represented in figure 6. The obtained average features' size of pristine

Table 2. The $R_{\text{rms}}$, size and height of surface features, aspect ratio, and power-law exponent values of pristine and irradiated KNN films.

| Samples                  | $R_{\text{rms}}$ (nm) | Size of surface features (nm) | Height of surface features (nm) | Aspect ratio | Power-law exponent (n) |
|--------------------------|------------------------|-------------------------------|---------------------------------|--------------|------------------------|
| Pristine                 | 10.6                   | 231 ± 10                      | 25 ± 3                          | 0.11         | 2.37 ± 0.01            |
| $1 \times 10^{12}$ ions cm$^{-2}$ | 4.9                    | 164 ± 9                       | 12                              | 0.07         | 1.85 ± 0.02            |
| $5 \times 10^{12}$ ions cm$^{-2}$ | 8.3                    | 248 ± 7                       | 19 ± 1                          | 0.08         | 2.22 ± 0.01            |
| $1 \times 10^{13}$ ions cm$^{-2}$ | 8.8                    | 247 ± 5                       | 22 ± 1                          | 0.09         | 2.25 ± 0.01            |

Figure 5. AFM images of (a) pristine KNN, and irradiated films at fluence of (b) $1 \times 10^{12}$ ions cm$^{-2}$, (c) $5 \times 10^{12}$ ions cm$^{-2}$, and (d) $1 \times 10^{13}$ ions cm$^{-2}$. 

Table 2. The $R_{\text{rms}}$, size and height of surface features, aspect ratio, and power-law exponent values of pristine and irradiated KNN films.
KNN film is 231 ± 10 nm, which is then decreased to 164 ± 9 nm after irradiation at 1 × 10^{12} ions cm^{-2}, and beyond this, it is further enhanced with an increase in ion fluence. The variation of surface roughness and size distribution of surface features with respect to ion fluence is depicted in figure 7. The surface roughness is found to vary in similar trend as that of average size with ion fluence. It can be perceived from AFM images that the areal density of surface features is increased at a fluence of 1 × 10^{12} ions cm^{-2} due to decrease in average size and, thereafter, is decreased monotonically with ion fluence due to the evolution of bigger surface features.

Initially, the reduction of average size may be due to the transfer of energy of incident ions by which adatoms might have moved on the surface, and thus, the height (shown in the inset of figure 6) and the size of surface features decreased at 1 × 10^{12} ions cm^{-2}. The similar results have also been reported for 50 MeV Ni ion irradiated ZnO thin films [26], and CdZnO matrix irradiated with 100 MeV Au ion beam [34]. As the fluence
increased beyond $1 \times 10^{12}$ ions cm$^{-2}$, the size of surface features and roughness both are increased with ion fluence. This can be due to the augmentation of mobility of adatoms, which induced the coalescence effect on the surface and thus increases the growth along vertical height as well as the lateral size of surface features [35]. During the coalescence process, the grain growth increases, and therefore, areal density decreases with ion fluence beyond $1 \times 10^{12}$ ions cm$^{-2}$. The concept of surface roughness can also be related to the aspect ratio of surface height to size of surface features. It is generally considered that the largest aspect ratio of surface features indicates the roughest surface for a given value of surface roughness [36]. From table 2, it is clear that the aspect ratio of average vertical height and average size of surface features of films is decreased at $1 \times 10^{12}$ ions cm$^{-2}$ and beyond that, it rises monotonously with ion fluence. The variation of aspect ratio of surface features is similar as that of change in $R_{\text{rms}}$ value with the ion fluence. As a result, the surface roughness of films is increased upon SHI irradiation beyond the fluence of $1 \times 10^{12}$ ions cm$^{-2}$ in the present study. Therefore, the modification in size of surface features and surface roughness might be due to the modification in surface energy after deposition of energy from heavily energetic ion beams. The irradiation induced morphological evolution study has also been reported by different research groups [15, 37, 38].

To understand the mechanism of surface evolution, a surface scaling study through power spectral density (PSD) analysis is employed. PSD analysis can be quite useful as it provides the quantitative representation of surface growth in both lateral and vertical directions, and it remains independent from the scan area of sample. The 2D-PSD function is quantitatively obtained from the Fourier transform of the surface and is defined as [15, 32]:

$$PSD(q) = \frac{1}{L^{2}} \left| \int \int d^{2}r e^{-i\mathbf{q} \cdot \mathbf{r}} \langle h(r) \rangle \right|^{2}$$ (2)

where $q$ is spatial frequency, $L$ represents the length of scan area, $h(r)$ is the surface height at a position $r = (x, y)$. The 2D-PSD curves of pristine and irradiated KNN films are shown in figure 8(a). AFM images of scan size $3 \times 3 \ \mu m^2$ are utilized for PSD analysis. The log-log plot of PSD spectrum shows two distinct spatial frequency regions; the horizontal low frequency region i.e., Region I, which corresponds to uncorrelated noise, while the tail of PSD curves in high frequency region i.e., Region II, resembles the correlated surface features. The significant parameters analogous to PSD curves are: (i) the slope of PSD curves in high spatial frequency region (at large $q$), which gives the predominant mechanism of surface evolution; (ii) correlation length $\xi_0$ ($=1/q_0$), which is related to the lateral surface roughness; (iii) the plateau height ($\omega$) in low frequency region, which defines the height of surface features. The horizontal part of PSD curve in a low value of $q$ depicts the stochastic roughening (as shown in figure 8(a)). Stochastic roughening may be opposed by the various lateral mass transport mechanism and assists in making the surface smoother. The analysis of tail of the PSD curve provides information about smoothening mechanism depending upon the slope of curve in high spatial frequency region.

The surface corrugation is described as the slope of lines joining two points on the surface, which becomes minute for length longer than that of correlation length $\xi_0$. The surface is considered to be flat for length greater than $\xi_0$. Therefore, for real-space behavior, it can be expected that the PSD should remain independent for $q < 1/\xi_0$, while it should decrease with an increase in $q$ for $q > 1/\xi_0$. The surface corrugation becomes significant for spatial frequency greater than $q_0$, and PSD displays the power-law dependence as [39]:
The induced effects of SHI irradiation on the surface morphology of KNN films were further analyzed by FESEM. The SEM micrographs and the grain size distribution of pristine and irradiated samples at different fluences of 1 × 10^{12} ions cm^{-2} depend on spatial frequency. Thus, the high spatial frequency region (Region II) is differentiated into three parts for better understanding. Most of the part of PSD function exhibits the smoothening of surface through viscous flow driven by surface tension, and this mechanism is sharply turned to volume diffusion with frequency. This might be the reason for decrease in size and height of surface features at fluence 1 × 10^{12} ions cm^{-2}. It is considered that the smoothening mechanism of viscous flow (n = 1) plays an important role in smoothening of oxide films [36]. The smoothening of the surface at fluence 1 × 10^{12} ions cm^{-2} can be explained from the cascade collision of ion-solid interaction. The energy acquired by surface atoms might be less as compared to that of surface binding energy; the adatoms may not leave the surface but can drift parallel to the surface and build the surface smoother.

The possible smoothening mechanisms are illustrated schematically in figure 8(b). The value of n is calculated from the linear fitting of PSD curve in region II (shown in figure 9) and is found to be 2.37 ± 0.01 for pristine KNN films. Upon irradiation, the value of n is decreased to 1.85 ± 0.02 at a certain fluence 1 × 10^{12} ions cm^{-2} and, thereafter, increases with ion fluence, although the variation is relatively small. So, the smoothening of surface for a fluence of 1 × 10^{12} ions cm^{-2}, evaporation-recondensation and viscous flow are the competing mechanisms of adatom motion for surface smoothening, and thereafter, the evolution of surface morphology is due to evaporation-recondensation and volume diffusion mechanisms. It is observed that the surface smoothening mechanism for films irradiated at 1 × 10^{12} ions cm^{-2} depends on spatial frequency. Thus, the high spatial frequency region (Region II) is differentiated into three parts for better understanding. Most of the part of PSD function exhibits the smoothening of surface through viscous flow driven by surface tension, and this mechanism is sharply turned to volume diffusion with frequency.

**Figure 9.** Plots of linear fitted PSD versus spatial frequency: (a) Pristine, irradiated KNN films at fluences of (b) 1 × 10^{12} ions cm^{-2}, (c) 5 × 10^{12} ions cm^{-2}, and (d) 1 × 10^{13} ions cm^{-2}.

The induced effects of SHI irradiation on the surface morphology of KNN films were further analyzed by FESEM. The SEM micrographs and the grain size distribution of pristine and irradiated samples at different fluences of 1 × 10^{12} ions cm^{-2} depend on spatial frequency. Thus, the high spatial frequency region (Region II) is differentiated into three parts for better understanding. Most of the part of PSD function exhibits the smoothening of surface through viscous flow driven by surface tension, and this mechanism is sharply turned to volume diffusion with frequency.

This might be the reason for decrease in size and height of surface features at fluence 1 × 10^{12} ions cm^{-2}. It is considered that the smoothening mechanism of viscous flow (n = 1) plays an important role in smoothening of oxide films [36]. The smoothening of the surface at fluence 1 × 10^{12} ions cm^{-2} can be explained from the cascade collision of ion-solid interaction. The energy acquired by surface atoms might be less as compared to that of surface binding energy; the adatoms may not leave the surface but can drift parallel to the surface and build the surface smoother.

The significant increase in surface roughness of KNN films beyond 1 × 10^{12} ions cm^{-2} ion fluence is assumed to be due to evaporation or sputtering of adatoms from the surface. From the PSD spectra, it is observed that the plateau height of curves vary with the fluence of ion beam irradiation. The decrease in w is observed at initial fluence (1 × 10^{12} ions cm^{-2}) while it increases at higher fluences. The decrease in w at 1 × 10^{12} ions cm^{-2} suggests that the surface roughness of films decreases. Thus, the nature of variation in w with ion fluences is similar to the Rrms of films. Therefore, ion induced evaporation-recondensation and viscous flow processes seem to play a dominant role in smoothening of KNN films irradiated at a fluence of 1 × 10^{12} ions cm^{-2}.

PSD(q) = Aq^{-n}; where A is a constant, and n denotes the power-law exponent and is related to the slope of tail of the PSD curve, which is a real number and predicts the mechanism of surface evolution. The surface transport mechanisms of surface features are relatively dependent on the numerical values of n, i.e., n = 1, 2, 3, or 4. The numerical value of n is related to different smoothening mechanisms such as viscous flow caused by surface tension, evaporation-recondensation, volume diffusion, and surface diffusion, respectively [36, 40].
fluences are depicted in figure 10. The pristine sample exhibits that the grains are arranged in regular manner with rod-like and spherical structures along with some irregular shaped features. Upon irradiation at $1 \times 10^{12}$ ions cm$^{-2}$, the morphology of sample remained similar with more homogeneity, but the average grain size is found to reduce from $215 \pm 8$ nm to $143 \pm 7$ nm. A further increase in ion fluence, the spherical and rod-like structure disappears, and grains are found in bigger size with a well-defined structure due to agglomeration under induced modification by SHI irradiation. The average grain size is found to be $232 \pm 6$ nm and $234 \pm 9$ nm for samples irradiated at ion fluences of $5 \times 10^{12}$ ions cm$^{-2}$ and $1 \times 10^{13}$ ions cm$^{-2}$, respectively. The increase in grain size with ion fluence is probably due to sudden enhancement of lattice temperature, which caused the coalescence with an increase in ion fluence [41]. The SEM results with variation in ion fluences are similar to AFM. Moreover, some pinholes and cracks on the surface of films also appeared in pristine sample as indicated by the arrow in figure 10(a), which might be due to the evolution of residual stress (compressive/or tensile) in films as an effect of post-annealing treatment [42]. The annihilation of these cracks and reduction in pinholes are found after subjected to ion beam irradiation. The strain relaxation behavior after irradiation with increasing ion fluence is also observed in XRD results where peaks shifted towards lower diffraction angle with ion fluence. In addition, small white regions can also be seen in the grain boundaries on the surface of samples, which indicates the evaporation of materials due to their volatilization behavior. This shows the presence of pyrochlore phase in the grain boundaries, which can be confirmed from the XRD results. Also, the large number of fragmented white regions in case of irradiation at $5 \times 10^{12}$ ions cm$^{-2}$ substantiated the increased amount of secondary phase. The presence of pyrochlore phases after crystallization in grain boundary regions is also observed for similar piezoelectric perovskite material [43]. Therefore, SHI irradiation led to modify the surface morphology of KNN films as a function of ion fluence.

4. Conclusions

We have investigated the modification of surface topography and structural properties of KNN thin films irradiated using a 100 MeV Ni ion beam. The systematic decrease in peak intensities of XRD after irradiation of films is observed. The average crystallite size of KNN films varies non-monotonously with ion fluence. The amount of secondary phases other than crystalline KNN is decreased at a fluence of $1 \times 10^{12}$ ions cm$^{-2}$, and at this fluence, the more pronounced orientation-(001) is enhanced. SEM images revealed the improvement in surface morphology of KNN films as a result of ion beam irradiation with increasing ion fluence. AFM analysis shows that films irradiated at $1 \times 10^{12}$ ions cm$^{-2}$ exhibits minimum surface roughness, and beyond this...
fluorescence. $R_{\text{rms}}$ value increases with fluence. Surface-scaling analysis of the AFM images gives a power-law exponent ‘n’ in range of 1.85 — 2.37 for pristine and irradiated KNN films. Irradiation at a particular fluence of $1 \times 10^{12}$ ions cm$^{-2}$ suggests the smoothening mechanism by a combined effect of viscous flow and evaporation-recondensation dominated processes. Further, the smoothening mechanism is found to shift towards the competitive process between evaporation-recondensation and diffusion processes for higher fluences. A strong correlation is found between the $R_{\text{rms}}$ size and height of surface features, their aspect ratio, and the power-law exponent value.

Acknowledgments

RS is grateful to UGC, New Delhi for providing UGC-SRF fellowship. AD acknowledges MHRD, Government of India, for fellowship during the research tenure. Authors are thankful to Inter-University Accelerator centre, New Delhi, for providing ion beam facility. The authors are highly thankful to Dr Fouran Singh, Materials Science Group, IUAC, New Delhi for experimental support, and fruitful discussion. We would like to thank Materials Research Centre, MNIT Jaipur, for the characterization facilities.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Pamu Dobbidi @ https://orcid.org/0000-0002-0834-8461
Srinivasa Rao Nelamarri @ https://orcid.org/0000-0003-0752-4336

References

[1] Saito Y, Takao H, Tani T, Nonoyama T, Takatori K, Homma T, Nagaya T and Nakamura M 2004 Lead-free piezoceramics Nature 432 84–7
[2] Samanta S, Sankaranarayanan V, Sethupathi K and Ramachandra Rao M S 2018 Enhanced ferroelectricity in PLZT ceramic by precise La-doping, minimizing pyrochlore phase and lead loss Vacuum 157 514–23
[3] Shibata K, Oka F, Oishi A, Mishima T and Kanno I 2008 Piezolectric properties of (K,Na)NbO$_3$ films deposited by RF magnetron sputtering Appl. Phys. Express 1 011501
[4] Kanno I, Ichida T, Adachi K, Kotera H, Shibata K and Mishima T 2012 Power-generation performance of lead-free (K,Na)NbO$_3$ piezoelectric thin-film energy harvesters Sensors Actuators A Phys. 179 132–6
[5] Mahesh P and Pamu D 2014 Structural, mechanical and optical properties of nanocrystalline (K$_{0.34}$Na$_{0.65}$)NbO$_3$$_{0.95}$ thin films deposited by RF sputtering J. Ceram. Sci. Technol. 5 23–30
[6] Goh P C, Yao K and Chen Z 2010 Lead-free piezoelectric (K$_{0.34}$Na$_{0.65}$)NbO$_3$ thin films derived from chemical solution modified with stabilizing agents Appl. Phys. Lett. 97 102901
[7] Wang L, Zuo R, Liu L, Su H, Shi M, Chu X, Wang X and Li J 2011 Preparation and characterization of sol-gel derived (Li,Ta,Sb) modified (K,Na)NbO$_3$ lead-free ferroelectric thin films Mater. Chem. Phys. 130 165–9
[8] Chua N T, You L, Ma J and Wang J 2010 Properties of (K,Na)NbO$_3$-based lead-free piezoelectric films prepared by pulsed laser deposition Thin Solid Films 518 6777–80
[9] Pop-Ghe P, Wolff N, Rubab A, Kienle L and Quandt E 2021 Tailoring growth modes by excess alkali addition in magnetron sputtered potassium sodium niobate thin films Mater. Today Commun. 27 102221
[10] Chao A 2010 Ion Beams in Nanoscience and Technology (Dordrecht: Springer-Verlag Berlin Heidelberg)
[11] Avasthi D K and Mehta G K 2011 Swift Heavy ions for Materials Engineering and Nanostructuring vol 145 (Dordrecht: Springer Netherlands)
[12] Jain I P and Agarwal G 2011 Ion beam induced surface and interface engineering Surf. Sci. Rep. 66 77–172
[13] Aumayr F, Facsko S, El-Said A S, Trautmann C and Schleberger M 2011 Single ion induced surface nanostructures: a comparison between slow highly charged and swift heavy ions J. Phys. Condens. Matter 23 393901
[14] Bharath Sabarish V, et al 2021 Influence of nickel (Ni$^{2+}$) Swift Heavy Ion (SHI) irradiation on the optical, topological, dielectric, piezolectric and ferroelectric properties of (011) oriented ferroelectric triglycine sulphate single crystals Chem. Phys. Lett. 769 138389
[15] Dash P, Mallick P, Rath H, Tripathi A, Prakash I, Avasthi D K, Mazumder S, Varma S, Satyam P V and Mishra N C 2009 Surface roughness and power spectral density study of SHI irradiated ultra-thin gold films Appl. Surf. Sci. 256 558–61
[16] Raghavan L, Joy P A, Vijaykumar B V, Ramanujan R V and Anantharaman M R 2017 Defect induced modification of structural, topographical and magnetic properties of zinc ferrite thin films by swift heavy ion irradiation Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms 396 68–74
[17] Saravanan R, Rajesh D, Rajasekaran S V, Perumal R, Chitra M and Jayavel R 2013 Structural, morphological and electrical studies of lithium ion irradiated sodium potassium niobate single crystal grown by flux method (AIP Conference Proceedings) pp 914–5
[18] Shyam R, Rathore M S, Vinod A, Das A, Dobbidi P, Singh F and Nelamarri S R 2020 Irradiation induced modification of structural and optical properties of potassium sodium niobate thin films Appl. Phys. A 1261
[19] Shyam R, Das A, Dobbidi P, Singh F, Vashishtha P, Gupta G and Nelamarri S R 2020 Improved optical properties of ion beam irradiated (K,Na)NbO$_3$ thin films J. Alloys Compd. 823 153794
[20] Dimaria D J and Kerr D R 1975 Interface effects and high conductivity in oxides grown from polycrystalline silicon Appl. Phys. Lett. 27 505–7
[21] Shyam R, Negi D, Vashishtha P, Gupta G, Das A, Dobbidri P and Nelamari S R 2021 Study of light-emitting defects induced by 100 MeV Ag ion irradiation in potassium sodium niobate thin films J. Lumin. 233 117909
[22] Toulemonde M, Dufour C and Paumier E 1992 Transient thermal process after a high-energy heavy-ion irradiation of amorphous metals and semiconductors Phys. Rev. B 46 14362–9
[23] Sharma A, Verma K D, Varshney M, Singh D, Singh M, Asokan K and Kumar R 2010 Effect of 100 MeV O$^{7+}$ ion beam irradiation on structural, optical and electronic properties of SnO$_2$ thin films Radiat. Eff. Defects Solids 165 930–7
[24] Cullity B D 1978 Elements of X-ray Diffraction (Reading: Addison-Wesley Publishing Company)
[25] Santhosh Kumar T, Vinod A, Rathore M S, Pathak A P, Singh F, Pamu D and Srinivasa Rao N 2018 Effects of high-energy ion-beam irradiation on structural and optical properties of (Mg$_{0.95}$Co$_{0.05}$)$_2$TiO$_4$ thin films Radiat. Eff. Defects Solids 173 128–37
[26] Kumar V, Singh R G, Purohit L P and Singh F 2013 Effect of swift heavy ion on structural and optical properties of undoped and doped Nanocrystalline Zinc Oxide films Adv. Mater. Lett. 4 423–7
[27] Jun B-E, Kim S B, Li G, Chun Choi B, Kee moon B and Hyun Jeong J 2010 Physical properties of $(1-x)K_{0.5}Na_{0.5}NbO_3-(x/3)NaK_2Li_2NbO_4$ composite ceramics Phys. Scr. T139 014033
[28] Ahn C W, Hwang H I, Lee K S, Jin B M, Park S, Park G, Yoon D, Cheong H, Lee H J and Kim I W 2010 Raman spectra study of $K_{0.5}Na_{0.5}NbO_3$ ferroelectric thin films Jpn. J. Appl. Phys. 49 095801
[29] Vendrell X, Raymond O, Ochoa D A, Garcia J E and Mestres I 2015 Growth and physical properties of highly oriented La-doped (K,Na)NbO$_3$ ferroelectric thin films Thin Solid Films 577 35–41
[30] Sharma S, Kumar A, Gupta V and Tomar M 2019 Dielectric and ferroelectric studies of KNN thin film grown by pulsed laser deposition technique Vacuum 160 233–7
[31] Mahesh P and Pamu D 2014 Effect of deposition temperature on structural, mechanical, optical and dielectric properties of radio frequency sputtered nanocrystalline (K,Na$_{x}$)$_3$Nb$_2$O$_7$ thin films Thin Solid Films 562 471–7
[32] Pétri R, Brasile P, Vatel O, Henry D, Andre E, Dumas P and Salvan F 1994 Silicon roughness induced by plasma etching J. Appl. Phys. 75 7496–506
[33] Rathore M S, Vinod A, Angalakurthi R, Pathak A P, Singh F, Thatikonda S K and Nelamari S R 2017 Ion beam modification of structural and optical properties of GeO$_2$ thin films deposited at various substrate temperatures using pulsed laser deposition Appl. Phys. A 123 708
[34] GuruSampath Kumar A, Soi Sarmash T, Obulapathi L, Jhansi Rani D, Subba Rao T and Asokan K 2016 Structural, optical and electrical properties of heavy ion irradiated CdZnO thin films Thin Solid Films 605 102–7
[35] Galdikas A 2006 Non-monotonous dependence of surface roughness on factors influencing energy of adatoms during thin film growth Surf. Sci. 600 2705–10
[36] Tong W M and Williams R S 1994 Kinetics of surface growth: phenomenology, scaling, and mechanisms of smoothening and roughening Annu. Rev. Phys. Chem. 45 401–38
[37] Abhirami K M, Matheswaran P, Goku K, Sathiyamoorthy R, Kanjilal D and Asokan K 2013 Effect of SHI irradiation on the morphology of SnO$_2$ thin film prepared by reactive thermal evaporation Vacuum 90 39–43
[38] Kumar V, Gupta R, Ram J, Singh P, Kumar V, Sharma S K, Katryar R S and Kumar R 2019 High energy 120 MeV Ti$^{7+}$ ion beam induced modifications in optical, structural and surface morphological properties of titanium dioxide thin films Vacuum 166 523–34
[39] Eklund E A, Bruinsma R, Rudnick J and Williams R S 1991 Submicron-scale surface roughening induced by ion bombardment Phys. Rev. Lett. 67 1759–62
[40] Herring C 1950 Effect of change of scale on sintering phenomena J. Appl. Phys. 21 301–3
[41] Nath D and Das R 2020 Phase transformation of CdSe nanocrystals at high flux irradiation of 120 MeV swift Na$^{10+}$ and Ag$^{+}$ ions—X-ray diffraction and Raman spectral analysis Appl. Surf. Sci. 509 144708
[42] Chandramohan S, Sathiyamoorthy R, Sudhagar P, Kanjilal D, Kabiraj D and Asokan K 2007 Swift heavy ion beam irradiation induced modifications in structural, morphological and optical properties of CdS thin films Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms 254 236–42
[43] Yeo H G and Trolle-McKinstry S 2014 [001] Oriented piezoelectric films prepared by chemical solution deposition on Ni foils J. Appl. Phys. 116 014105