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Nano/micro surface structural study of swift heavy ions irradiated PVDF Films by AFM

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The surface topography, structure and surface mechanical properties of pristine and energetic ion irradiated PVDF films have been investigated using Atomic force microscopy (AFM) in trapping mode. The Polyvinylidene fluoride (PVDF) polymer films (9, 12 and 20 μm) were irradiated with 100 MeV Ag-ion (fluence; $1.8X10^{11}$ ions/cm^2), and 75 MeV Oxygen- ion (fluences; $5.6X10^{11}$ ions/cm^2, $1X10^{12}$ ions/cm^2 and $5.6X10^{12}$ ions/cm^2) beams with different beam currents ranging from 0.2-0.5PnA(particle nanoampere) using the PELLETRON facility at Inter University Accelerator Centre, New Delhi to study ion irradiation effects on the surface of thin films.
The AFM micrographs show the presence of small granular microstructure in pristine as well as irradiated PVDF samples. The AFM morphological characterizations of irradiated films reveal the formation of nano sized crater and hillocks on the sample surface. The AFM is also used to estimate average surface roughness, hardness, grain size, grain density and other structural parameters. The average surface roughness and grain size decreases after ion irradiation and the decrease dependents on the ion species, ion energy, ions beam current and fluences. However the grain size is more in lower energy ion (Oxygen-ion) irradiated samples than higher energy ion (Ag-ion) irradiated samples. Hall-Petch effect has been observed in PVDF thin films after ion beam irradiation i.e., increase in hardness of PVDF films upon ion beam irradiation.
Keywords: PVDF, SHI, AFM, TMAFM, TEM, PnA

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1. Introduction

The high energy heavy ion also termed as swift heavy ion (SHI), irradiation is a relatively new technique for tailoring the surface structure of polymeric material for specific technological applications including nuclear and space. The energetic ion when traverse through the polymeric material it losses its energy either in displacing atoms by elastic collisions (known as nuclear stopping) or ionizing the atoms by inelastic collisions (electronic stopping). The former is the dominant process at low energies whereas the inelastic collisions dominate at high energies where the displacements of atoms due to elastic collisions are insignificant. The energy thus deposited causes various surface structural modification in the material. The interaction of SHI with PVDF will change its surface structural properties. It has been recognized that the surface structural properties of PVDF influence its many other properties such as adhesion, friction, biocompability, crystallinity, wettability etc.

The PVDF is a semi-crystalline high molecular weight polymer with $–CH_2-CF_2-$as repeating unit and exhibits unique piezoelectric, pyroelectric, ferroelectric, and nonlinear optical properties, which promote its use in many technological applications including sensors , actuators, nonlinear optical component and ferroelectric memory[1-4]. In addition to its high piezoelectric coefficient, the advantages such as flexibility, bio-compatibility, lightness, and low acoustic and mechanical impedance make PVDF a favorable material for implantable medical devices, micro actuators [5].

The PVDF is also one of the rare polymer having at least five phases known as α, β, γ, δ and ε [6-8]. Earlier reports have shown that the α- phase comprises of helical structure with chain conformation- trans-gauche-trans-gauche' (TGTG'), while β- phase posses all-trans planar zigzag conformation. The PVDF in its β- phase show piezo- and pyroelectric properties, and hence become the focus for various transducers applications.

The behavior of PVDF irradiated to different types of ions has been studied by several groups [9-16]. These studies reveal the enhancement in electrical conductivity and change in crystallinity of PVDF [9, 10-14]. The decrease in crystallinity has been reported under electron and low-energy ion irradiation [10-12] whereas an increase in crystallinity has been reported under electron, X-ray and γ-ray irradiations [9, 12-15]. The crystallinity plays a crucial role in determining piezoelectric, mechanical, optical, electrical and even thermal properties of polymers [10]. The SHI irradiation effect on the surface properties of various polymers have been studied with scanning tunneling microscope (STM) scanning electron microscope (SEM) and transmission electron microscope (TEM), but the surface morphological investigations of

SHI irradiated PVDF thin films are not yet fully explored. Atomic Force Microscopy (AFM) technique is preferred over TEM and SEM techniques for investigation of morphology and nanometer-scale structure of polymeric thin film. Because TEM and SEM techniques require elaborate sample preparation, while no sample preparation is required for AFM to investigate nanoscale structural feature near the surface of the sample.

The aim of the present work is to investigate the surface microstructual and other properties, on scales of few micron to nanometers, of PVDF thin films of different thicknesses before and after irradiation with 100 MeV Ag-ion and 75 MeV Oxygen- ion beams at different fluences using Atomic Force Microscopy (AFM).

2. Experimental details

The poly-vinylidene fluoride used in the present study was procured form DuPont (USA) in film form of thicknesses 9 μm, 12 μm and 20 μm. The samples of size 1 sq. cm were mounted on a ladder for the irradiation in a vacuum chamber. The ladder was loaded in a chamber kept in a high vacuum of the order of 10^{-6} Torr. The films were then irradiated with 100 MeV Ag-ion beam at fluence $1.8X10^{11}$ ions/cm^2 (beam current of 0.2 PnA) and with 75 MeV Oxygen-ion beam at fluences; 5.6×10^{11} ions/cm^2, 5.6×10^{12} ions/cm^2 (beam current of 0.5 PnA) and 1×10^{12} ions/cm^2 (beam currents of 0.2, 0.5 PnA) using the PELLETRON facility at Inter University Accelerator Centre (IUAC), New Delhi. The ion beam fluence was measured by integrating the ion charge on the sample ladder with time. Ion energies were selected in such a manner that they can easily pass through the PVDF films. The depth profiles were estimated using SRIM calculations. The projected range of 100 MeV Ag-ion, 75 MeV Oxygen- ion beams in the PVDF was calculated to be 25.55 μm and 105.35 μm respectively, using the SRIM-08 code (Ziegler 2008), which are larger than the thickness of PVDF samples.

The pristine and SHI irradiated PVDF films were later investigated by AFM techniques. The Solver PRO 47 (NT-MDT, Russia) scanning probe microscope operating in the semi contact mode (Trapping mode) was used. Images were acquired using 'Golden' silicon probes (NTMDT, Russia) with resonance frequencies of 260 kHz (tip radius of 10 nm). All measurements were performed with the instrument mounted in a vibration isolation system (figure1). The scanning probe microscope is also used to estimate the surface roughness. A series of scanning shots were taken from different parts of sample surface.

3. AFM investigations

Atomic force microscopy (AFM) is the member of the family of advance surface analysis techniques know as scanning probe microscopy (SPM) and has been turned out to be indispensable tool for investigation of surface morphology**,** nano/microstructure, mechanical and other properties of polymeric material. An AFM can be used in different modes for producing the topographic image of the sample surface. The AFM operation in trapping mode is preferred, for obtaining high resolution topographic images, as it avoid damage to the tip and sample surface caused by physical rubbing. Trapping mode atomic force microscopy (TMAFM) is of particular interest in determining topography and phase morphology of polymer films. In tapping mode, the silicon probe tip oscillates at its resonance frequency as it rasters across the sample surface and experiencing only intermittent contact with the surface. The surface topography is represented by the height image in TMAFM. Following the surface morphology, constant oscillation amplitude is used as the feed back signal via the z displacement of the piezo-ceramics. The amplitude image is obtained by recording the variation of the root mean square (RMS) of the amplitude before the feedback loop. In this mode the lateral resolution is around one nanometer.

4. Results and discussion

The AFM micrographs of pristine and 100 MeV Ag-ion (fluence; 1.8×10^{11} ions/cm^2) irradiated PVDF films of different thicknesses (9 μm, 12 μm and 20 μm) are shown in figures 2 and 3 respectively, while the AFM micrographs of 20 μm PVDF film irradiated with 75 MeV Oxygen-ion (fluences; 5.6×10^{11} ions/cm^2, 1×10^{12} ions/cm^2 and 5.6×10^{12} ions/cm^2) are shown in Fig. 4 (a), (b), (c) and (d). We have illustrated both two dimensional as well as three dimensional AFM images of the pristine and irradiated samples. Analysis of a topographic AFM images allows us to obtain the size histogram of the grains, grain density '**h**', their mean size '**d**' and their size dispersion. The roughness and other structural parameters measurement results of the analyzed AFM micrographs of pristine and irradiated samples are reported in Table 1.

Table 1. Roughness and other structural parameters measurement results of pristine and SHI irradiated PVDF samples of different thicknesses (9 µm, 12 µm and 20 µm).

Samples → / Properties ↓	Pristine			100 Mev Ag-ion irradiated (fluence 1.8×10^{11} ion/cm^2)			75 Mev oxygen - ion irradiated (fluence; 5.6×10^{11} ion/cm^2)	75 Mev oxygen - ion irradiated (fluence; 1.6×10^{12} ion/cm^2) (0.2 PnA)	75 Mev oxygen - ion irradiated (fluence; 1×10^{12} ion/cm^2) (0.5 PnA)	75 Mev oxygen- ion irradiated (fluence; 5.6×10^{12} ion/cm^2)
Thickness of samples → (µm)	9 µm	12 µm	20 µm	9 µm	12µm	20µm	20 µm	20 µm	20 µm	20 µm
Average grain size(d) (nm)	17.7	18.4	18.3	16.0	13.0	12.0	13.4	12.4	13.8	14.0
Average Roughness, Sa (nm)	16.07	4.17	26.58	7.99	3.98	3.99	16.95	0.80	46.9	12.53
Root Mean Square, Sq (nm)	20.54	5.62	35.82	10.57	5.19	5.41	21.17	0.96	59.7	17.18
Crystallinity (%)	48.3	52.56	51.53	44.53	50.28	48.5	53.69	51.12	48.5	47.08

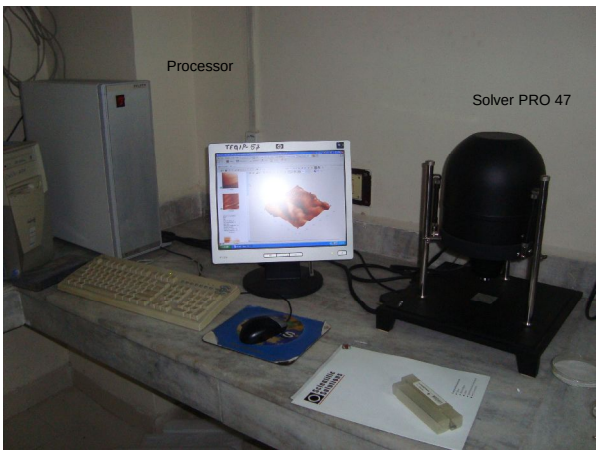


Fig. 1. AFM experimental setup.

The roughness parameters are defined as:

(i) **S_q** (Root Mean Square roughness parameter) is the standard deviation of the Z values within a given area and calculated by the equation:

$$S_q = [\sum_i (Zi - Zav)^2 / N]^{½} \quad (1)$$

where Zav is the average of the Z values within the given area, Zi is the current Z value, and N the number of points within the given area.

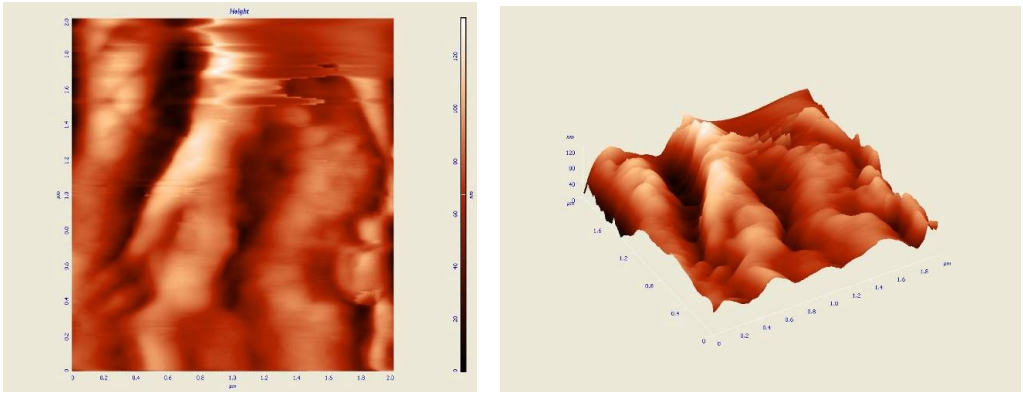
(ii) S_a is the mean surface roughness. This is the mean value of the surface relative to the centre plane and is calculated using following relation;

$$S_a = 1 / Lx .Ly \int_{Ly} \int_{Lx} | f(x, y) | dx\, dy \quad (2)$$

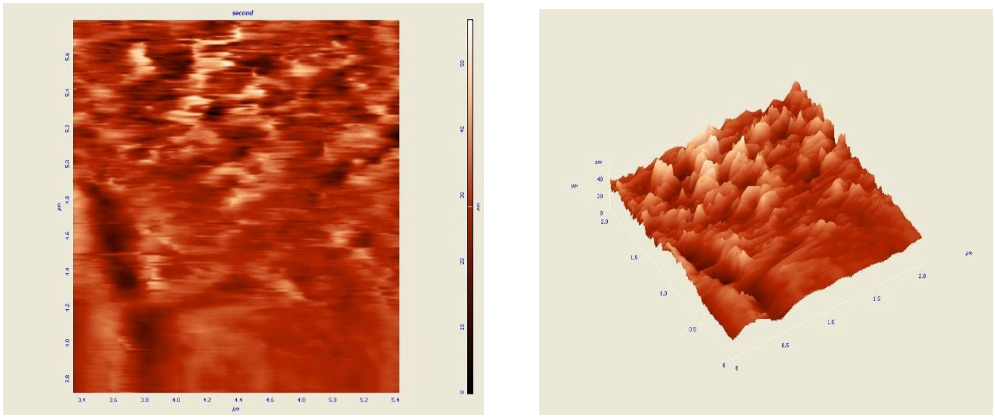
where f(x, y) is the surface relative to the centre plane and Lx and Ly are the dimensions of the surface.

The AFM micrographs (Fig. 2) of pristine PVDF films show that the surface of samples has different morphological patterns. Our earlier FTIR and XRD analysis [6] of the pristine as well as irradiated PVDF samples have shown the presence of α-, β-, and γ- phases. The different patterns in AFM micrograph can be

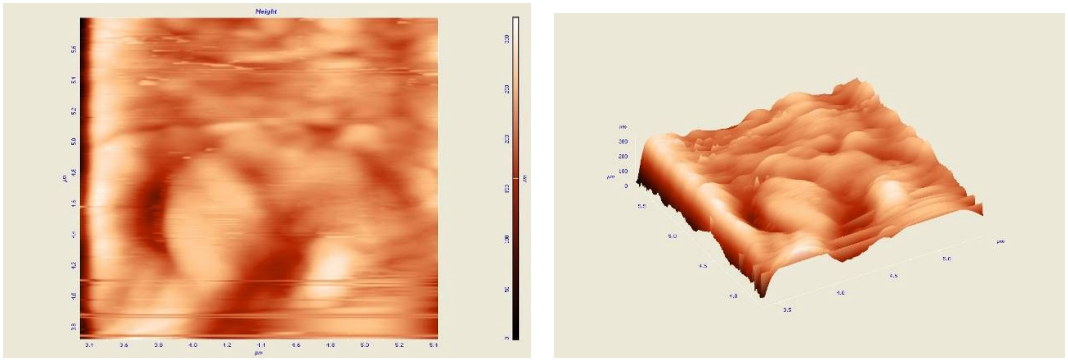
associated with these phases. At least two different morphological patterns (white and dark) are easily identified in every AFM micrographs of pristine samples. All pristine PVDF samples show granular nano/microstructure matrix with granular grains inlaid on this matrix. The three dimensional AFM images of pristine samples show mountain features with sharp valleys at the bottom.



(a) 9 µm



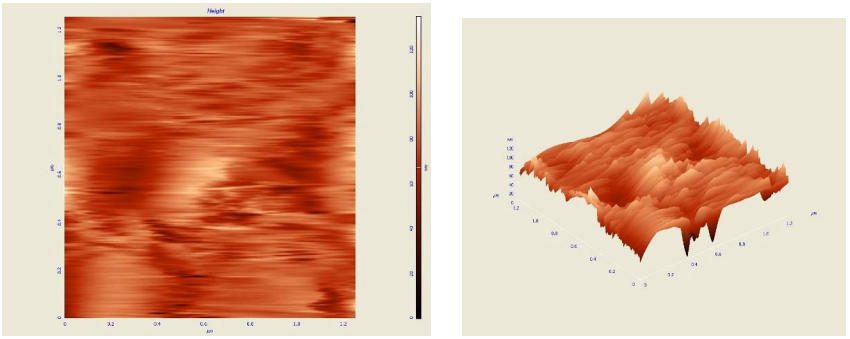
(b) 12 µm



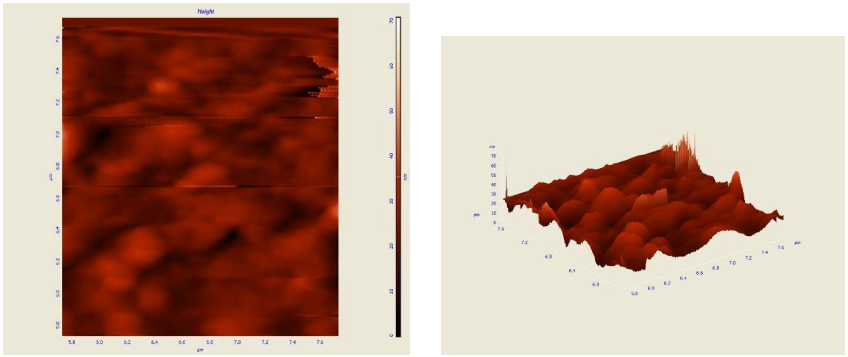
(c) 20 µm

Fig. 2. AFM micrograph for pristine PVDF films (a) 9 µm (b) 12 µm (c) 20 µm.

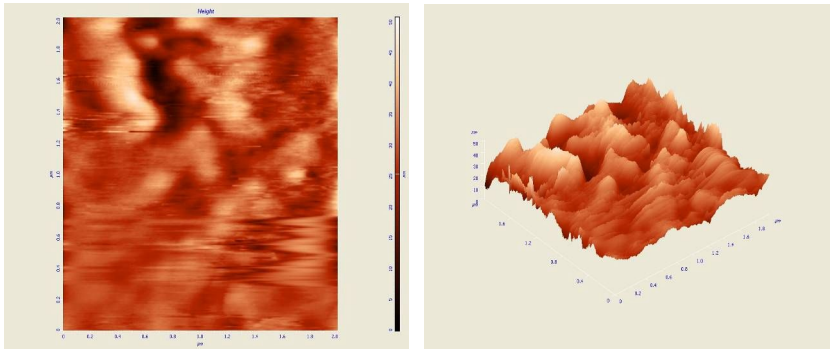
The AFM micrograph (Fig. 3) of Ag-ion irradiated PVDF samples also show granular nano/microstructure with different kind of grains. We can also observe some small craters-hillocks at the edge of micrographs. The formation of hillocks in the present case has been attributed to nuclear energy loss induced collision cascades which take place near the surface and are responsible for displacement of atoms forming clusters. The Ag-ion irradiated PVDF samples show decrease in average surface roughness S_a (Table 1). The average surface roughness, S_a decreases drastically in case of 20 µm irradiated PVDF sample which suggests the smoothening of surface and this relative smoothness is probably due to the sputtering effects.



(a) 9 µm



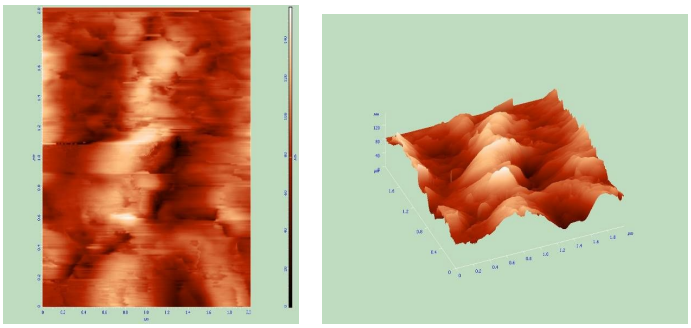
(b) 12 µm



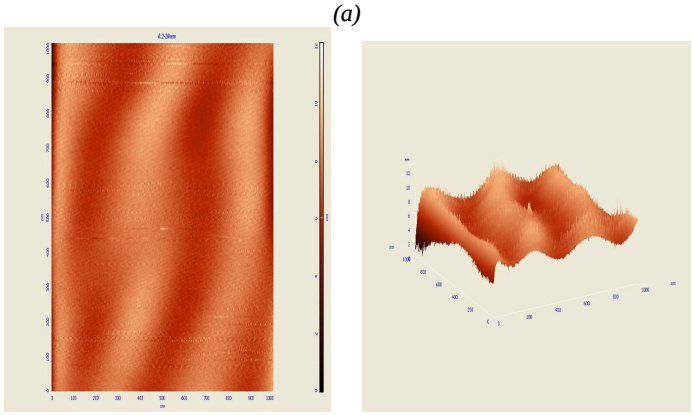
(c) 20 µm

Fig. 3. AFM micrograph for Ag-ion irradiated PVDF films (a) 9 µm (b) 12 µm (c) 20 µm.

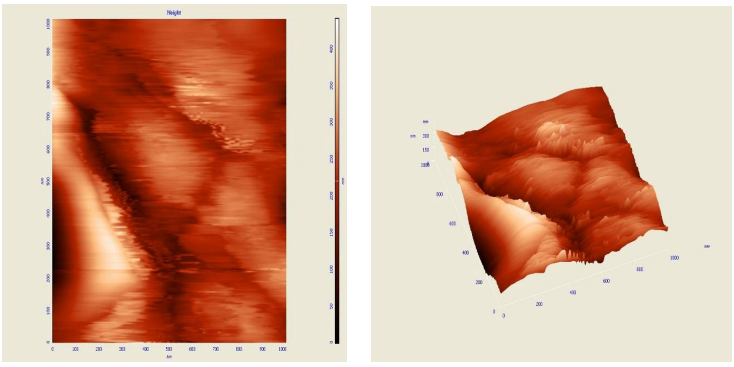
The decrease in S_a is also observed in 20 µm PVDF samples irradiated with 75 MeV Oxygen-ion. Interestingly the S_a also observed to be fluence dependent. The S_a decreases significantly in high fluence irradiated sample. Further the AFM micrograph show the abundance of hillocks in Ag-ion irradiated PVDF samples as compare to Oxygen-ion irradiated samples at higher PnA. It appears that LETs (Linear Energy Transfer) associated with these ions are responsible for this behavior. The SRIM calculation show that nuclear LET of Ag-ion is nearly hundred times more the nuclear LET of Oxygen ion for this polymer. This confirms our earlier observation that nuclear energy loss mainly responsible for the formation of hillocks. We also observed crater in lower fluence oxygen ion irradiated sample. It is interesting to observe large numbers of very small hillocks in 20um film irradiated with Oxygen-ion beam with lower beam current 0.2 PnA than the higher beam current 0.5PnA for the same fluence; $1X10^{12}$ ions/cm^2 (Fig. 4 (b) and (c)). This may due to the sputtering effect at the lower PnA, which is also reflect from the drastically decrease in average surface roughness S_a data. One of very significant aspect which reveled by the 3D, AFM micrograph of Oxygen-ion irradiated PVDF is about the fluence dependent crystalline behavior of this polymer. The micrograph clearly show an enhancement in crystallinity in low fluence Oxygen-ion irradiated sample where as in high fluence irradiated sample a decrease in crystallinity as compare to pristine sample. The same is also depicted in crystallinity data given in the Table 1. In polymer, the change in behavior in crystallinity with fluence has been associated to the occurrence of secondary radiation induced crystallinity (SRIC) [17]. This change of crystallinity behavior with fluence can be associated with the occurrence of SRIC.



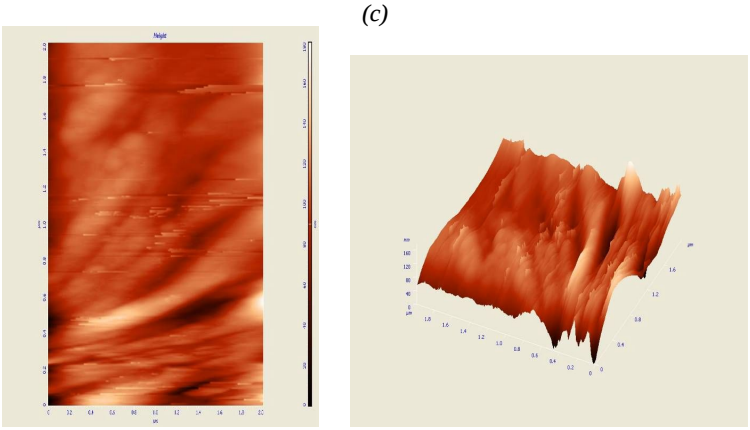
(a)



(b)



(c)



(d)

Fig. 4. (a) AFM micrograph for 20 µm Oxygen-ion irradiated (at fluence 5.6 ×10^{11} ions/cm^2)PVDF film; (b) AFM micrograph for 20 µm PVDF film irradiated by Oxygen-ion beam with beam current 0.2 PnA (fluence; 1×10^{12} ions/cm^2); (c) AFM micrograph for 20 µm PVDF film irradiated by Oxygen-ion beam with beam current 0.5 PnA (fluence; 1×10^{12} ions/cm^2); (d) AFM micrograph for 20 µm Oxygen-ion irradiated (fluence; 5.6 ×10^{12} ions/cm^2) PVDF film.

The AFM study also show that the average grain size (d) decreases upon SHI irradiation and further decrease in grain size is observed at lower fluence. Table 1 show that decrease in average grain size (d) in ions irradiated samples is dependent on thickness of samples. It is well know that the grain size of the material influences its hardness properties. Classically, one would expect an increase in hardness (H) for the decrease in grain size in ion irradiated samples according to the Hall-Petch equation [18-19] given below;

$$H = H_0 + K\, d^{-1/2} \qquad (3)$$

where H_0 is the lattice friction stress in the absence of grain boundaries, K is constant and 'd' is the grain size. The hardness of SHI irradiated films is strongly dependent upon ion energy, beam current, fluence and ion species [20]. It appears that Ag-ion irradiated samples show more improvement in hardness than the Oxygen-ion irradiated samples. This improvement in hardness can be associated with different LETs of these ions. The SRIM calculation show that nuclear LET of 100 Mev Ag-ion is nearly hundred times more the nuclear LET of 75 MeV Oxygen-ion and the electronic LET of 100 Mev Ag-ion is nearly ten times more the electronic LET of 75 MeV Oxygen-ion for this polymer.

5. Conclusions

The surface morphology of pristine and heavy ion irradiated PVDF thin films have been investigated using Atomic Force Microscopy. The roughness values such as average roughness, S_a, root mean square roughness, S_q, and other physical parameters such as crystallinity, grains size of pristine and irradiated samples have been estimated. The average surface roughness S_a, and grain size (d) is influenced by ion energy, beam current, fluence and ion species. Improvement in hardness of SHI irradiated samples is associated with the different LETs of ions.

The AFM micrographs show occurrence of nano sized crater and hillocks in irradiated PVDF films**.** The formation of nano sized crater and hillocks is dependent on the ion species, ion energy, ions beam current (PnA) and fluences. Both pristine and SHI irradiated films demonstrate amorphously nanocrystalline composition. The surface morphology of films deteriorated at the higher fluence.

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