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NANO/MICRO SURFACE STRUCTURES BY SWIFT HEAVY ION IRRADIATION OF POLYMERIC THIN FILMS ON GaAs

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In this paper creation of nano/micro sized surface structures by ion irradiation on polymeric surface coated on GaAs substrate is presented. Generally ion beam passing through a medium causes various modifications and changes in properties of the matrix. Here thin polymeric films (polycarbonate, 10μm) spun coated on GaAs substrates were irradiated normally (to the substrate) with 50 MeV, Ni^{+11} and 150Mev, Li^{+3} ion beam. Later AFM and SEM morphological characterizations reveal the nano/micro sized hillocks and crater on the surface. The nature and the shape of the hillocks indicate that the diffusion of gasses formed during irradiation can be attributed as the main cause for these surface modifications.

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Keywords: GaAs, Surface structure, Heavy ion irradiation, Thin Film, AFM, SEM

1. Introduction

Swift heavy ions lose energy in materials mainly through inelastic collisions with the atomic electrons. Along the trajectory of ion, a trail of defects known as latent track may be formed depending on the type of the ion, its energy as well as the physical property of the materials. This damage is always created in the close vicinity of the trajectory of the projectile. The energy of the projectile is transferred to the atom through excitation and ionization of the surrounding electrons.

A surface track defined as the portion of a material that is modified or perturbed in response to the energy deposited by an individual ion (or a cluster) penetrating a solid. Three main features are often distinguished in a surface track; a region of lattice disorder, a hole or crater and a region of raised material with dimensions of the order of nanometers. In certain materials only humps are seen at the impact site and in others only rimless craters are present. The size and morphology of surface tracks depend on rheological and thermal properties of polymer in a symmetric way [1-3]. This surprising behavior is of interest because surface tracks can be registered in a region of a few nanometer areas. This raises the possibility of using single-ion tracks not only as a tool for tailoring nanostructures on the surfaces but also to study the changes induced along ion tracks.

Generally ion irradiation causes scission and cross-linking of polymeric chains that usually alter the molecular weight, structure and composition of the polymer [7,8]. One of the most important chemical changes related to chain scission on a polymer is the release of free radicals and gases emitted after ion irradiation; the released gases are usually H_2, CH_4, CO, CO_2 and CN [9]. Along with chain scission, the incident ions create great amounts of defects when they collide with the target atoms or molecules. Here in this paper we have irradiated polymer-coated semiconductors and there AFM and SEM analysis shows the presence of swollen hillock and crater like structures on the surface.

2. Experimental procedure

The Preparation of substrate was carried out at Inter University Accelerator Center (IUAC), New Delhi, India, and the CSIO, Chandigarh, India. To remove the dirt and oxide layer from the surface of the semi conducting substrate GaAs (P-doped) (111), wafer was dipped in Trichloroethylene, acetone and methanol for 10 min each in succession followed by dipping in 10% hydrochloric acid for 1 min. Finally, the wafer was rinsed with deionized water for 5 min. A thin layer of polycarbonate (Makrofol) was deposited onto substrate by spin coating and the thickness of polymer was around 10μm. The adhesion of the polycarbonate film on the substrate was improved by the use of a primer (hexamethyldisilazane HMDS). The prepared samples were irradiated (with ion beam falling normally on the sample) with 150 MeV Ni^{+11} and 50MeV Li^{+3} ions at fluencies of 2E7 ion/sqcm using the ion beam facility at 15UD Pelletron accelerator IUAC, New Delhi, India. Incidence ion energy is chosen in such a way that the ion crosses the polymeric layer and penetrates the substrate. Before and after irradiation, the samples were characterized using AFM and SEM.

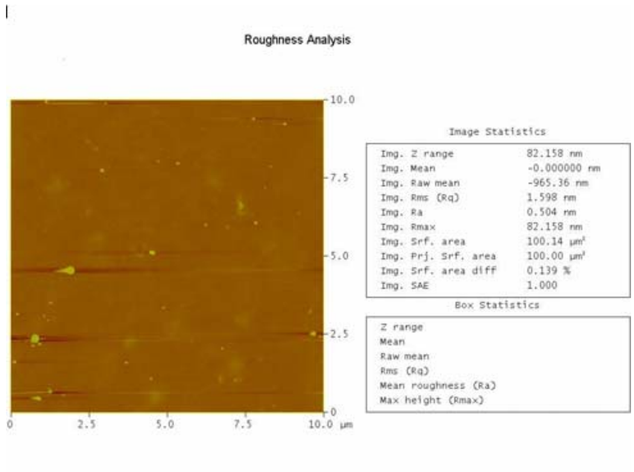
From SRIM 2008 calculations S_e and S_n for 150 MeV Ni ions is 4.18E+01 MeV/(gms/cm^2) and 4.98E-02 MeV/(gms/cm^2) respectively with projected range of the order of about 36.43 um which is more then twice the thickness of polymeric layer, so may be easily concluded that the ion must have penetrated the semiconducting substrate and got trapped in it. And for 50 MeV Li ions S_e and S_n about 5.25E-01 MeV/(gms/cm^2) and 2.89E-04 MeV/(gms/cm^2) respectively and projected range 451.09 um. With S_e/S_n ratio as 839.3 and 1816.6 respectively.

SRIM 2008 program shows that the Li ions with 50 MeV energy not only cross the polymeric layer even it crosses the 0.5mm thick GaAs substrate. But Ni ions are stopped on their way at a distance of about 15μm.

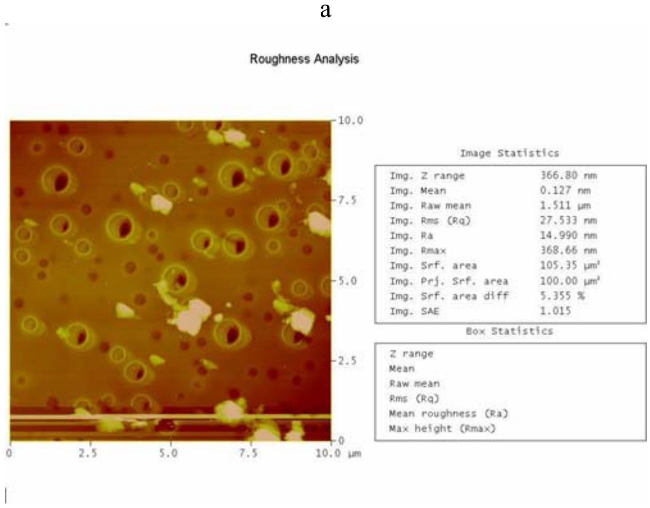
3. Results and discussion

A series of typical AFM (Nanoscope IIIa) image in height mode is shown in Fig. 1. Pictures of pristine samples Fig 1 (c) and ion-irradiated samples Fig 1 (a) and (b) clearly distinguishes the crates and heights (hillocks) on the surface. It is well known that when an energetic ion passes through a medium it leads to various types of damages to the matrix. These damages are generally not noticeable but the modification caused on the surface can help in detailed study of ion beam effect on insulators. 3-Dimensional view of these samples shows that these structures are of nano dimensions Fig 2 presents the same. Li ion irradiated samples show some hillocks along with craters on the surface but Ni ion-irradiation creates hillocks only. From Fig 3(a) showing the section analysis, depth of the crater is near about 100 micrometers and from Fig 3(b) height of hillock is near about 10 micrometers.

Craters and hillocks formation in swift heavy ion bombardment of polymer surfaces is a very interesting phenomenon. Different models have been proposed to explain the mechanism behind these surface modifications in polymers. Among them, the pressure-pulse model, the thermal-spike model and the shock-wave model, are widely used [4-5]. In the pressure-pulse model, the angular distributions of target molecules are asymmetrical and diffusion causes the propagation of the energy density resulting from the ion-solid interaction in the solid. It's a hydrodynamic type model. The thermal-spike model assumes that the energy is transported in the solid due to heat conduction; the energy deposited by the incident ion creates a thermal spike characterized by a temperature. Finally the third model, namely the shock-wave model, suggests that the target molecule redistribution is due to the propagation of shock wave that is caused by the sudden pressure change in the ion-bombarded region. This model describes the ability of shockwaves arising from latent tracks to lead to compacting of the region around the ion track or according to this model when an ion penetrates the foil it creates shockwaves around its path [6]. All three models take into consideration the energy transfer from the ion to the solid but only the first model treats the energy transfer through transportation of mass in the solid. However, mass transport is very important in understanding the crater or hillocks formation mechanism. The mechanisms of craters-hillocks formation are still unclear the main reason behind is the complex structure and composition of polymeric materials.



a



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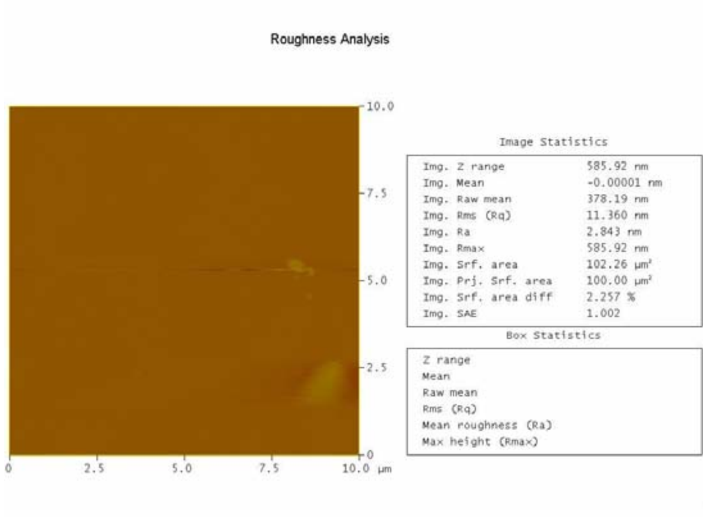

c

Fig 1. AFM images of (a) 150 MeV Ni (+11) ion irradiated samples, (b) 50 MeV Li (+3) ion irradiated ion irradiated samples and (c) AFM image of pristine sample

The interaction between projectile and the target material depends on the velocity of the projectile, which is the decisive parameter for the stopping of energetic particle in the matter. Heavy ions that possess kinetic energy higher than 1MeV/amu are slowed down in matter primarily by ionization of the target atom with the emission of secondary electron with high kinetic energy and by excitation of electronic system of the target. As a major fraction of this high energy is transferred to thermal energy causing local increase in temperature. The registration of ion tracks is a consequence of several secondary processes, occurring due to relaxation of electronically deposited energy into the lattice system of the target material. This may include bond breaking, atomic displacements, heat conduction, shock waves propagation, phase changes etc. The changes induced depend on the target material as well as on various beam parameters such as charge, energy, mass and fluence of the incoming projectiles and can result in well-ordered patterns, such as ripples or self ordered dots [14-16] Surface modification in materials like in insulators,[17-22] semiconductors,[23-25] and metals[26,27] due to ion (single) irradiation has been studied using, scanning electron and atomic force microscopes. A variety of features have been observed like: hillocks [25], craters [17-21], crater rims [17-21]. Cratering occurs as a response of pressure pulse and fluid flow produced by the rapid deposition of energy, but the process is not understood quantitatively. Hillocks generally appear when an energetic process occurs just bellow and very near to the surface, creating a low-density region with a larger volume which raises the surface [28]. Impact of single ions has been demonstrated to induce nano-sized hillocks on metals, semiconductors and dielectric targets ([16,29] and Refs.Therein)

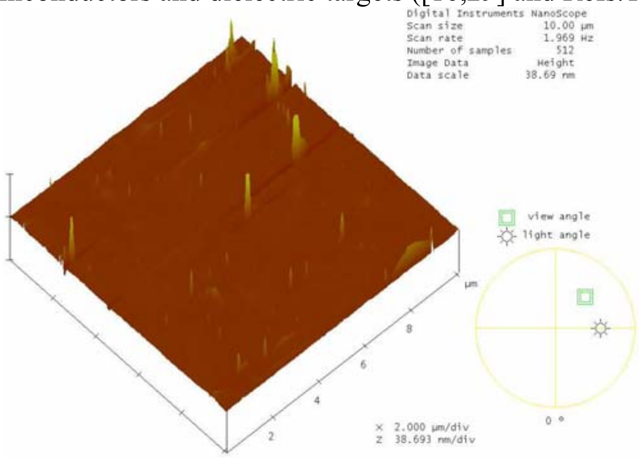

Fig 2(a) 3D-AFM image of Ni ion irradiated asmples

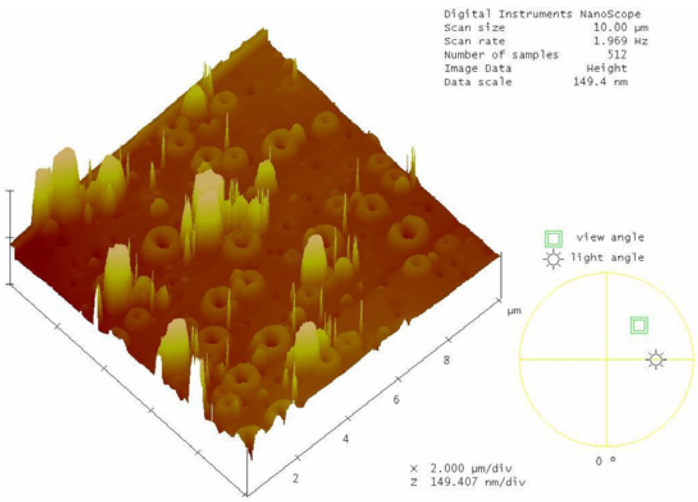

Fig 2(b). 3D AFM image of Li ion irradiated samples

Previous research on ion-bombarded polymer shows that the gases like H_2, CH_4, O, CO_2 etc. are released in the target. Along the path incident ions apart from creating a large amount of defects due to the result of chain scission in polymer, gases like H_2, CH_4, O, CO_2 etc. are released. [30-33]. Fig (4) giving the SEM images of irradiated samples, the number of the hillocks per unit area was found to be in good agreement with the applied ion fluence. Generally hillocks are accompanied with craters but from the section analysis and SEM pictures we can see that these hillocks don't have any crater near to them. This behavior is different from general results but can be explained on the basis of diffusion of gases formed during irradiation of polymer. As suggested by D. He and M. N. Bassim [34] the basic process in the proposed model by this group involves the diffusion and trapping of gases, forming bubbles on the surface, breaking of blisters with gas release, and eventual formation of craters on the surface. Over here for the Ni ion irradiated samples no craters are formed shows that the pressure caused by released gasses, during irradiation is less then the strength of the upper layer. Initially, incident ions create great amounts of defects and cause chain scission, which releases free radical gases (Fig. 5(a)). The incident ions may also capture electrons to become gas atoms or gas molecules. But in our case incident ion must have crossed the polymeric layer and stopped in semi-conducting substrate (for Ni ion) as the range of the incident ion beam is more then the thickness of polymeric layer (SRIM-TRIM 2008). These gases diffuse in the polymer and are trapped by defects to form bubbles (Fig. 5(b) and 5(c)). While the concentration of the gas builds up, the coalescence of bubbles forms blisters (Fig. 5(d)). The internal pressure on the surface can cause further surface deformation and eventually breaks the blister leading to crater formation at the ion impact site (Fig 5(e)), the one we have observed for the case of Li ion irradiated samples. This difference in surface modifications of same samples when irradiated with different ions may be attributed to the difference in the S_e/S_n ratio, which is more for the case of Li ion showing that electronic energy loss (causing direct energy momentum and transfer along the ion path), dominates the nuclear electronic loss (including inelastic collisions).

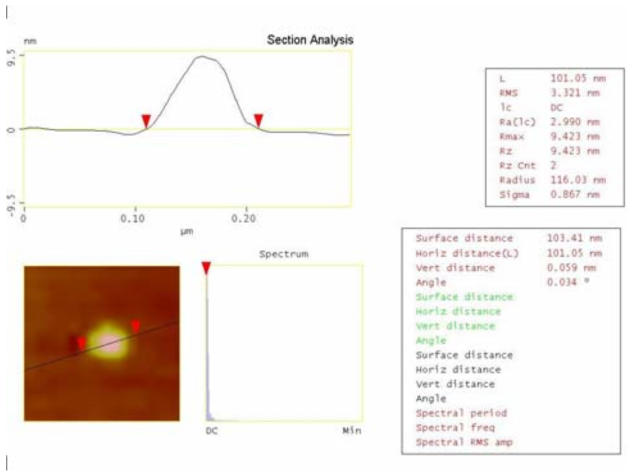

Fig 3(a). Section analysis of Ni ion irradiation samples.

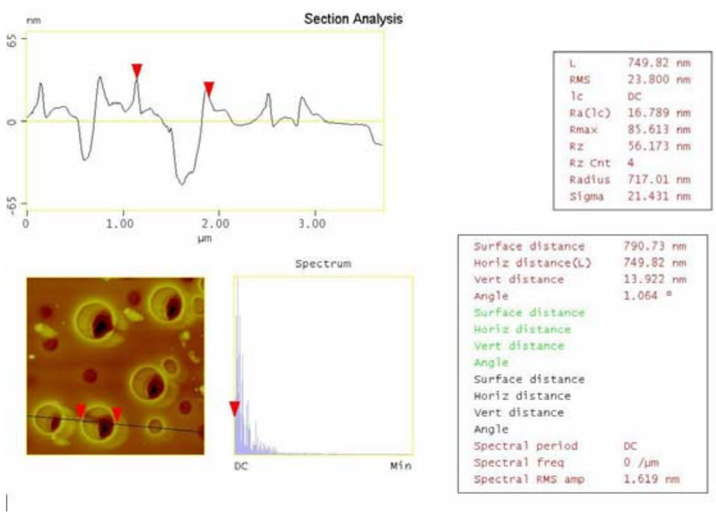

Fig 3(b). Section analysis of Li ion irradiation samples.

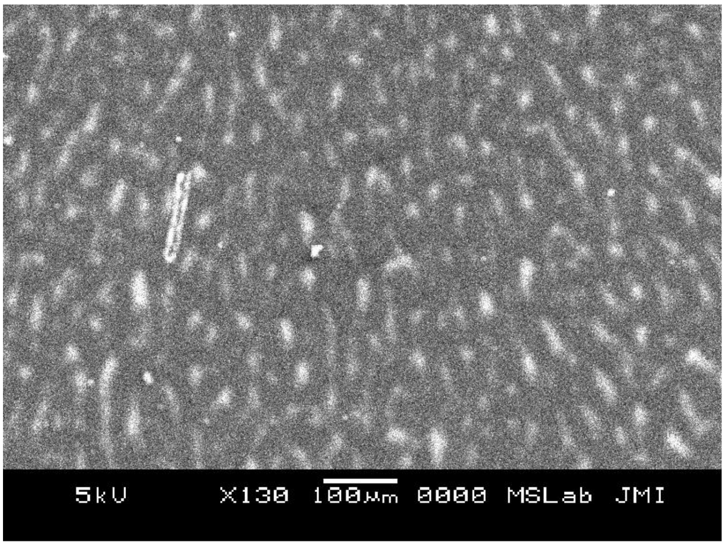

Fig 4(a). SEM image of the polymer coated GaAs samples irradiated with Ni ions

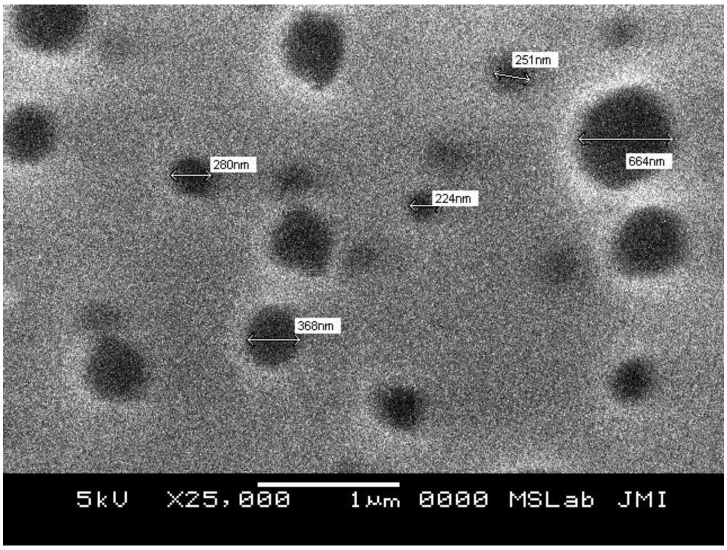

Fig 4 (b). SEM image of the polymer coated GaAs samples irradiated with Li ions

Fig 1(a) shows the AFM image of the Li ion irradiated samples showing the presence of some crater like structures with specific rim along the circumference along with few height (hillocks), on the surface This pattern formation is surprisingly similar to what is observed after heating thin polymer films on semi-conductor substrates above their melting point and also in metal oxide coated semi-conducting film bombarded with swift heavy ions. Especially, the larger holes exhibiting bright rims are of more interest, while for the smaller holes no such circular boundaries can be seen. There are present some elevated regions these may be the regions where less energy is deposited by the incident ion leading to hillocks only but not there further evolution as craters. The holes or so-called craters are surrounded by the rim like structures with heights up to 35 nm and are of asymmetric height. Further, they also show relatively increasing steep at inner side and a slow decay on the rear side of the rim, as can be seen in the section analysis shown in the fig 3.

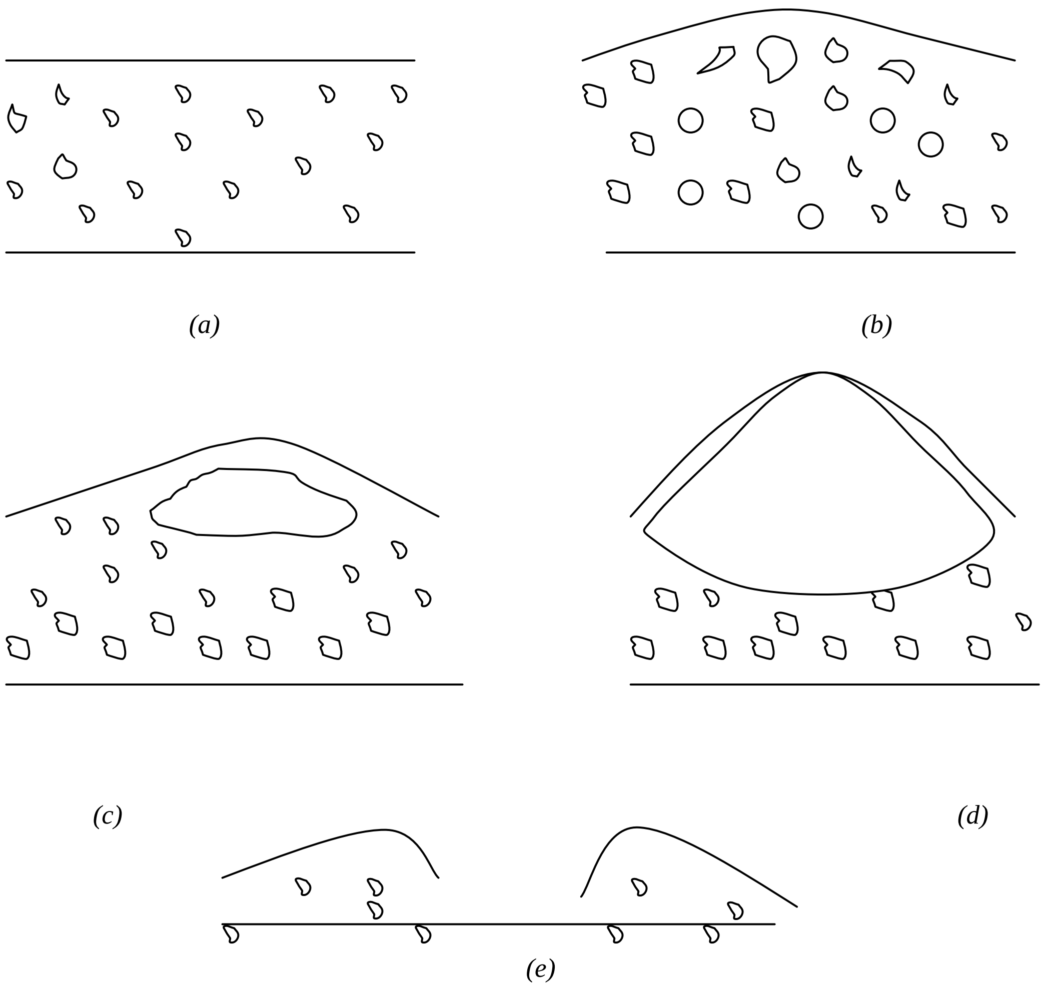

Fig 5: Drawing of crater formation on an ion-bombarded polymer: (a) un-irradiated sample surface; (b) defects created by ions; (c) gas trapped by defects to form bubbles; (d) surface deformation caused by bubbles (hillocks); (e) blister formed by the coalescence of bubbles (crater)

4. Conclusions

Impact of swift heavy ions is known to induce physical, chemical, and structural modifications not only on the surface but also in the bulk [35-37]. Individual projectiles form cylindrical tracks around their trajectory of a few nanometers in diameter. Track formation sets in above a critical value of the energy loss dE/dx of the projectiles and occurs particularly in insulators (e.g. polymers, oxides, ionic crystals). The present study suggests that diffusion and trapping of gas molecules and gas atoms in an ion-bombarded polymer may be the fundamental cause of observed craters and hillock formation on polymer surface. And the difference in S_e/S_n radio may give different structural modifications for same samples under same conditions. These surface structures are stable in atmosphere at room temperature. The study of these structures is interesting, as they are one of the important phenomena-taking place in early stages of track formation. By changing the parameters like energy temperature substrate and fluencies we can further explore this process. However visualization and study of as-induced surface modifications and defects without surface treatment using techniques like Atomic force microscopy (AFM), scanning tunneling and transmission electron microscopes can help in study of ion solid interaction and for its further application involving ion beam technologies.

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