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Full Length Article

Surface structuring in polypropylene using Ar^+ beam sputtering: Pattern transition from ripples to dot nanostructures

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ABSTRACT

Temporal variations in nano-scale surface morphology generated on Polypropylene (PP) substrates utilizing 40 keV oblique argon ion beam have been presented. Due to controlled variation of crucial beam parameters i.e. ion incidence angle and erosion time, formation of ripple patterns and further its transition into dot nanostructures have been realized. Experimental investigations have been supported by evaluation of Bradley and Harper (B-H) coefficients estimated using SRIM (The Stopping and Range of Ions in Matter) simulations. Roughness of pristine target surfaces has been accredited to be a crucial factor behind the early time evolution of nano-scale patterns over the polymeric surface. Study of Power spectral density (PSD) spectra reveals that smoothing mechanism switch from ballistic drift to ion enhanced surface diffusion (ESD) which can be the most probable cause for such morphological transition under given experimental conditions. Compositional analysis and depth profiling of argon ion irradiated specimens using Rutherford Backscattering Spectroscopy (RBS) has also been correlated with the AFM findings.

1. Introduction

In recent years, ion beam sputtering (IBS) has established itself as a versatile tool which offers unique and fascinating capabilities for fabrication of wide range of surface topographies at nanometer and micron length scales, with large number of technological applications as optical devices, templates for liquid crystal orientation and strain-free patterned substrates for hetero epitaxial growth of quantum dots or wires [1–4]. However, Slepicka et al. have constructed the micro- and nano-patterned surfaces over bio-polymers by the irradiation of the materials with plasma discharge treatment [5–7]. Biological functionality of solid state substrates was significantly improved and can be used as tissue scaffolds with specific functions regarding cell adhesion and proliferation or potential biosensor applications [8,9]. While Moon et al. created three-dimensional structures on the surface of the polymers by adopting the maskless patterning method of the focused ion beam system [10].

In particular, during ion beam sputtering, the solid surface is driven far from equilibrium and complex interplay between a variety of atomic scale processes such as surface roughening (induced by curvature-dependent sputtering) and surface smoothing processes (induced by surface relaxation mechanisms) become effective [11]. The competition between such atomistic processes results in evolution of some nano-scale patterns over the surface of amorphous material, as suggested by Bradley and Harper (BH) [12]. In contrast, if surface smoothing processes predominate during the sputtering process, it can lead to emergence of ultra-smooth surfaces, explored recently by Frost et al. [13]. Moreover, based on experimental parameters and choice of target material, unique possibilities for different type of surface morphologies under ion beam erosion can come into existence.

Up to now extensive experimental and theoretical work has been undertaken to study the effect of ion beam sputtering on the various semi-conductors [1,2,14,15] and other materials [3,4,16]. But the potential of this technique is still not well explored in this direction for the polymeric matrices and detailed understanding of the phenomenon is still far from complete. In this regard, to extend and understand the use of IBS for topographical evolutions over polymeric surfaces, experiments have been performed recently by our group in which surface smoothing as well as surface rippling has been attained simultaneously [17]. Due to their versatile characteristics, polymeric materials are gaining importance world-wide in numerous fields of science and technology [18].

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After our initial experiments in this direction, this is the first report regarding our recent findings on topographical transition from ripple patterns to the dot like pattern on Polypropylene (PP) surfaces induced by 40 keV Ar^+ ion irradiation. In particular, it is demonstrated that ion beam erosion leads to powerful surface smoothing along-with evolution of self-organized surface morphology which undergoes transition depending upon crucial beam parameters. Based on the experimental parameters used in the present study, theoretical estimations in terms of evaluation of B-H coefficients and analysis of PSD spectra have been carried out in order to reveal the underlying physical processes causing the observed pattern transition.

2. Experimental details

PP substrates used in this work were procured from M/S Goodfellow Cambridge Ltd. (Huntingdon, England). Specimens of area $1.5 \times 1.5\ cm^2$ were cut from the 500 μm thick optically flat PP sheet and were irradiated to 40 keV Ar^+ ions utilizing 200 kV Ion Accelerator facility available at Ion Beam Centre, Kurukshetra University, Kurukshetra, India. A low beam current density 1 μA cm^{-2} was maintained under a vacuum of $\sim 2 \times 10^{-7}$ Torr to achieve the fluences of $1 \times 10^{16}\ Ar^+\ cm^{-2}$, $2.5 \times 10^{16}\ Ar^+\ cm^{-2}$ and $5 \times 10^{16}\ Ar^+\ cm^{-2}$ at various off normal incidences of 30°, 40° and 50°. Specimens were mounted on the aluminium holder with the help of double sided carbon tape on all the four sides and beneath the sample surface to limit sample charging.

The near surface topography of the pre- and post-irradiated specimens was examined using Atomic Force Microscope (AFM), in semi-contact mode. The average depth and width of energy deposition of incoming ions in irradiated specimens have been calculated using SRIM simulations [19].

Rutherford Backscattering Spectrometry (RBS) also has been employed for depth profiling of the incident argon atoms in the surface layers of the PP material. RBS spectra of irradiated specimens were measured utilizing a beam of 2.0 MeV He^+ ions at scattering angle of 165° with 1.7 MV Pelletron accelerator at Inter University Accelerator Centre, New Delhi.

3. Results and discussions

3.1. Investigation of surface morphology after oblique argon beam treatment

Fig. 1(a-j) presents the two dimensional AFM micrographs in scan area of $5 \times 5\ \mu m^2$ of un-irradiated and 40 keV Ar^+ sputtered specimens at various incident angles as 30°, 40° and 50° w.r.t surface normal and fluences varying from $1 \times 10^{16}\ Ar^+\ cm^{-2}$ to $5 \times 10^{16}\ Ar^+\ cm^{-2}$. The microscopic analysis of these AFM images in terms of wavelength and amplitude of polymeric surface ripples (obtained through section analysis of respective AFM images of Fig. 1) have been calculated using NOVA-Px software and are presented in Table 1.

It can be seen clearly from Table 1 that surface roughness (R_{RMS}) has been reduced drastically from 8.23 nm in case of un-irradiated specimen to 3.35 nm (with $1 \times 10^{16}\ Ar^+\ cm^{-2}$ at 30°) and this further reduces with increase in ion fluence and oblique incidence, reaches finally to 1.28 nm (with $5 \times 10^{16}\ Ar^+\ cm^{-2}$ at 50°) with simultaneous formation of nano scale patterns which is an important outcome from technological aspect. This significant smoothing of polymeric surfaces can be attributed to the sputter erosion of random features of rough amorphous polymeric surfaces. Roughness of pristine polymeric surfaces has been realized as a decisive factor for IBS induced nano-scale surface morphology in PP matrices as it assist the ion beam to skip the process of initial surface roughening for local curvature development and hence leads to formation of ripple patterns at lower ion fluence as compared to metallic or semi-conducting targets [20]. The variations in rms roughness as a result of argon ion irradiation at different experimental conditions are presented in Table 1 and plotted in Fig. 2.

Moreover simultaneous smoothing and structuring of polymeric surfaces have been attributed to the oblique ion irradiation induced erosion of random features of rough amorphous polymeric surfaces. Also, the formation of smooth ripple patterns observed as a result of argon irradiation can be attributed to the formation of lower molecular weight fragments due to polymeric chain scission and subsequent swelling [17].

Auto-correlation images also have been inserted in corresponding AFM micrographs (Fig. 1(a-j)) which reveal the formation of ordered ripple patterns at 30° off normal incidence. Ripple parameters such as ripple wavelength and amplitude have been found to decrease with increase in ion fluence (Table 1). This experimental finding has been accredited to the pre-dominance of surface smoothing mechanisms over curvature dependent surface roughening processes during prolonged sputtering times. Further, the increase in incidence angle to 40° leads to distortion in these ripple structures as well as change in their orientation and finally to random ordered nano-dot morphology at 50°. Due to higher depth of energy deposition (a) (Table 2) at lower oblique incidence of 30°, projected argon ions are capable to transfer much of their energy beneath the material surface which lead to the formation of ripple like patterns. But at higher incidences, energy transfer is comparatively lesser to produce ripples and cascade remains closer to the surface. Moreover, at this energy regime, inelastic losses are sufficient to produce electronic excitation and ionization of carbon atoms present at the surface of material [17].

These electronically excited species may get cross-linked together and form carbon clusters which appear in the form of nano-dots. With increase in ion fluence, uniform distribution of nano dots with reduced size and highest number density has been observed (Table 1) as shown in Fig. 2.

3.2. Theoretical description to understand the underlying mechanisms

To understand the cause of such sputtering induced surface morphology, we have adopted the following linear continuum equation proposed by BH [11]:

$$\frac{\partial h}{\partial t} = -\vartheta_0 + \vartheta_0 \frac{\partial^2 h}{\partial x^2} + S_x \frac{\partial^2 h}{\partial x^2} + S_y \frac{\partial^2 h}{\partial y^2} - K\left[\frac{\partial^4 h}{\partial x^4} + \frac{\partial^4 h}{\partial y^4}\right] \tag{1}$$

Here h is the height surrounding an arbitrary point during ion beam erosion in the small slope limit, ϑ_0 is the erosion velocity of an unperturbed, second term describes the lateral movement of the structures on the surface. While third and fourth terms represent the effective surface tension generated by the erosion process and the last term is the surface relaxation rate due to thermal effects. The BH coefficient S is a function of ion energy, ion incidence angle and the material properties and is given as

$$S_{x,y} = \frac{Ja}{N} Y_0(\alpha_{ion})\Gamma_{x,y}(\alpha_{ion}) \tag{2}$$

In given equation, J is the flux of incoming ions and Y_0 is the angle dependent sputtering yield of an initial flat surface. $\Gamma_x(\alpha_{ion})$ and $\Gamma_y(\alpha_{ion})$ coefficients account for the local variations and can be expressed as:

$$\Gamma_x(\alpha_{ion}) = \frac{A}{B_1}\sin\alpha_{ion} - \frac{B_2}{2B_1}\left[1 + \frac{A^2}{2B_1}\right]\cos\alpha_{ion} - \frac{AC}{B^2}\left[3 + \frac{A^2}{B_1}\right]\cos\alpha_{ion} \tag{3}$$