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THE USE OF FOCUSED ELECTRON AND ION BEAMS FOR THE FUNCTIONALIZATION AND NANOSTRUCTURING OF POLYMER SURFACES

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Abstract- Polymers are nowadays actively used in numerous applications owing their low cost and optimized structural properties. Besides, the miniaturization of the novel materials down to nano and even atomic scale needs the use of Electron Microscopy techniques both for imaging and structuring abilities. When used for surface modification, electrons and ions allow altering the surface properties towards special material designs. This study mainly focuses on investigation, optimization and modification of polymers' surface properties by the use of electron and ion beam treatment assisted by gas enhanced etching processes in FIB-SEM dual-beam platforms. Direct electron/ion beam etching and XeF_2 assisted etching were applied on high density polyethylene (HDPE), Melinex® and polypropylene (PP) samples, in order to obtain different forms of functionalized surfaces. The alterations in the surface properties provided by electron/ion beam and gas assisted modification processes were examined using complementary advanced analysis techniques, such as HR-SEM and AFM.

Keywords- Focused Ion Beams, Nanostructuring, Polymers, Functionalization, Electron Microscopy, Surface Modification

I. INTRODUCTION

Electron and ion beams can be used for surface structuring processes, besides their characterization based applications. When electrons and ions are maintained in the form focused beams in a dual-beam system, such structuring abilities are at very high definition ranges; varying from micrometers down to a few nanometers of resolution.

FIB-SEM (focused ion beam–scanning electron microscope) platforms are capable of multi-tasking on a large spectrum of materials varying from metals to biological samples in terms of imaging, chemical analysis, micro/nano-structuring, etching, deposition and prototyping [1-5].
When attached with gas injection systems (GIS), electron and ion based processes are assisted by gases that are often in the form of organometallic precursor molecules for deposition and etching gases for enhancing the milling rate of the materials. However, it should be noted that charged particles lead to irradiaton damage resulting in the degradation of materials which are subjected to beams in the form of ion implantation, amorphization, redeposition, mass loss and sputtering, especially in the case of ion exposure [6].

When irradiation damage can be controlled and tuned, it is well possible to turn the drawbacks into advantage. FIB-SEM platforms are versatile tools for applying specific doses of electrons and ions (also may be coupled with process gases) for the targeted procedures of modification and functionalization of material surfaces. The use of dual-beam platforms allows nanostructuring of surfaces precisely within pre-defined parameters and geometries determined by patterns provided by special software.

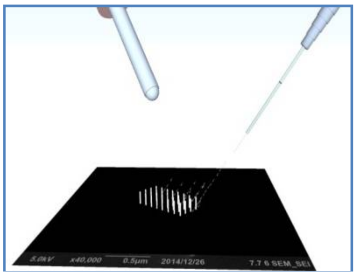

Fig.1. Beam assisted deposition via GIS unit.

This study concerns the use of focused electron and ion beams for the nanostructuring, and thus modification and functionalization of different polymer surfaces. Direct electron/ion beam exposure and XeF_2 assisted etching were applied on high density polyethylene (HDPE), Melinex® and polypropylene (PP) samples, in order to obtain different forms of functionalized surfaces. For determining the alterations in the surface properties (e.g. chemical, physical and morphological) after gas assisted electron and ion beam modification processes, HR-SEM and AFM characterization were carried on the polymer samples.
This work, in terms of methodology, is considered to be novel for literature, since it combines both the irradiation and gas assisted etching of polymer surfaces locally and simultaneously in a FIB-SEM platform. Former studies also show the effects of electron and ion irradiation on polymer surfaces and their use in a positive way [3], [7]-[11], however none of the previous work were performed using the patterning capabilities of dual-beam platforms.

II. DETAILS EXPERIMENTAL

In this study, three types of polymer materials were used for the surface modification experiments: high density polyethylene (HDPE), Melinex® (a type of polyester film) and polypropylene (PP). In order to avoid surface charging effects, the samples were sputter coated with conductive 10-20 nm thin films, such as carbon, platinum and gold. This was followed by placing the coated polymer samples on pin-stubs. The samples were then taken into FIB-SEM dual-beam platforms to carry out ion/electron beam assisted etching and irradiation experiments by applying different doses of beams and using various instrumental parameters. In addition to electron and ion beam irradiation effects, the morphological alterations caused by gas enhanced etching processes were simultaneously observed by the HR-SEM imaging mode. The experimental work in this study was performed in FEI NanoLab Dual-Beam, JEOL JIB MultiBeam and TESCAN Lyra FIB-SEM platforms. Besides, Atomic Force Microscopy (AFM) helped monitoring the fine morphological and topographical alterations on the polymers surfaces precisely, which are in the level of nano- and subnano- scale, as the outcomes of the beam and gas assisted surface modification processes. In this study a Bruker Multimode AFM system was used, while imaging was done using PeakForce QNM® mode. Compatible with the AFM mode, Bruker RTESPA-300 AFM tip was preferred. Gwyddion 2.40 and NanoScope Analysis 1.40 SPM imaging software were for processing the final images.

2.1. Surface Modification of Bulk HDPE Samples

HDPE, being widely used in daily life for many purposes ranging from packing to electronics, was chosen as a first polymer candidate in this study for surface modification experiments. Material surfaces were exposed to ion (gallium) etching and XeF_2 assisted ion (gallium) etching within 50x50 μm^2 square patterns by applying different ion doses and gas exposure times.

2.2. Surface Modification of Melinex® (polyester) Film Samples

Another surface modification study was carried out on Melinex® (polyester) films. Taking into accunt their high biocompatibility among all other polymer species, Melinex® films are commonly preferred for biological and medical applications. In this work, the surface modification effects of different ion currents were examined on Melinex® films for direct and gas assisted ion etching. Two ion currents were chosen (1 nA and 3 nA) for ion etching experiments which are considered to be moderate ion values for FIB and widely used for milling processes while 60 s, 120 s and 480 s was determined as the processing times within 50x50 μm^2 square patterns.

In addition, a comparative XeF_2 assisted electron irradiation work was performed in Melinex® polymer films for the use of 5 nA and 10 nA electron currents and 60 s, 120 s and 240 s processing times within 50x50 μm^2 square patterns, resulting in different electron doses.

2.3. Surface Modification of Bulk PP Samples

Used in various branches of industry, PP was chosen as another polymer candidate in this work for tracking the effects of beam induced surface modification. PP surfaces were exposed to ion (gallium) etching and XeF_2 assisted ion (gallium) etching within 50x50 μm^2 square patterns by applying different ion doses and gas exposure times. Preliminary experiments showed that there was no significant change which was observed in case of applying 1 nA ion current for varying doses of irradiation. For this reason, in this work, only the ion dose series for 3 nA was presented.

III. RESULTS AND DISCUSSION

3.1. HDPE Samples

The SEM and AFM topography images of pristine HDPE are given in Figure 2. AFM imaging was targeted to be performed in order to monitor the surface morphology at high definition, exposing all details of the modification processes.

The SEM and AFM topography images of pristine HDPE surfaces are given in Fig. 2. A comprehensive AFM analysis was performed in order to track the surface morphology at high resolution and in detail. The images reflect the homogeneity of the surface structure, as both using SEM and AFM, they were taken from the identical regions. It was observed that bulk HDPE polymer surfaces have a characteristic morphology and topography; however no original repeating texture was monitored for this sample.

Following this, the effects of different ion current was investigated on the HDPE surfaces for a constant gallium ion dose of 6,3 x 10^{17} ions/cm^2 determined for patterns with 50x50 µm processing areas. It has been found that no significant morphological difference was observed in the case of modification by gallium irradiation using 3 nA ion current (Fig. 3).

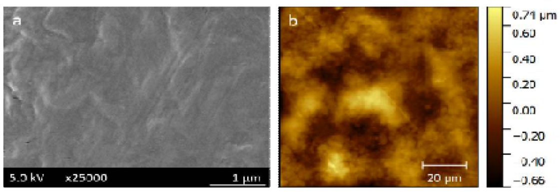

Fig.2. (a) HR-SEM SE and (b) AFM topography images of pristine HDPE surfaces.

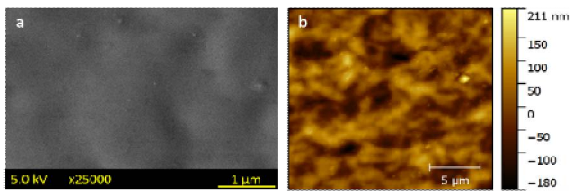

Fig.3. (a) HR-SEM SE image and (b) AFM topography image of HDPE surfaces after direct gallium irradiation using 3 nA resulting in the ion dose of 6,3 x 10^{17} ions/cm^2.

The morphology and topography differences in case of using XeF_2 etching gas for 3 nA, 5 nA and 7 nA ion currents were investigated for the constant ion dose and the corresponding SEM and AFM analysis was performed on the regions of interest, which are presented in Fig 4 and 5. In this irradiation series since the ion dose was kept constant and the ion current was altered; only the differences for the gas exposure times were monitored. In this case, because the processing time is the higher for the lower ion doses, durations were calculated as 840 s, 504 s and 360 s for 3 nA, 5 nA and 7 nA ion currents, respectively.

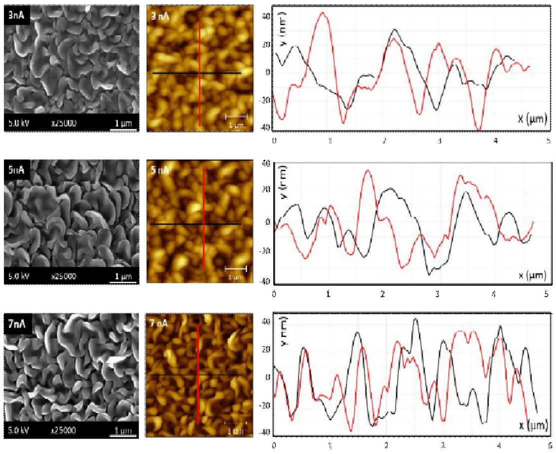

Fig.4. HR-SEM SE, AFM topography images and AFM surface profiles of HDPE surfaces after XeF_2 assisted ion etching using 3 nA, 5 nA and 7 nA resulting in the ion dose of 6,3 x 10^{17} ions/cm^2.

According to the findings it can be presumed that XeF_2 assisted ion etching leads to the formation of typical and repeating "warm-like" structures. The surface profiles helped revealing the nanometer scale deviations in the surface topography.

3.2. Melinex® Samples

The SEM image, AFM topography and AFM adhesion map taken from the surfaces of pristine Melinex® samples are given in Fig. 5. In can be observed in the images that the surface has a repeating elliptic texture in the micron size.

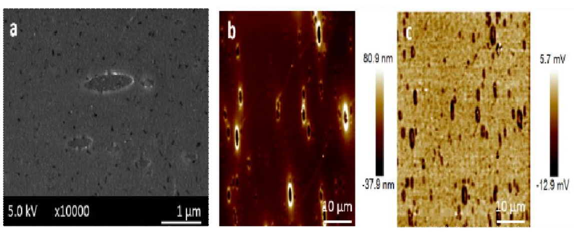

Fig. 5. (a) HR-SEM SE and (b) AFM topography (c) AFM adhesion map images of pristine Melinex® surfaces.

Fig. 6 shows the he SEM images of XeF_2 assisted ion etching of Melinex® foils. It can be suggested from the results that, the higher the amount of Ga+ implantation with the application of 3 nA ion current, the less the surface roughness and hence the original texture starts to vanish.

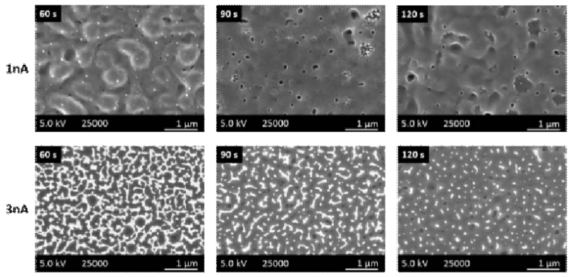

Fig. 6. SEM-SE images of XeF_2 assisted ion milling of Melinex® foil surfaces.

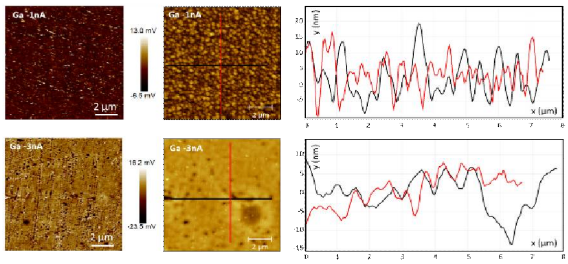

Fig. 7. QNM mode AFM adhesion maps, AFM topography images and corresponding surface profiles of ion etched Melinex® foil surfaces treated using 1nA and 3nA ion beam currents.

Fig. 7 and Fig. 8 show the QNM mode AFM adhesion maps, AFM topography images and corresponding surface profiles for monitoring the morphological differences on the Melinex® for direct gallium and XeF_2 assisted gallium etching. For this irradiation series, 30 keV ion energy and ion beam currents of 1 nA and 3 nA were used for the ion etching and GAE processes. 50x50 μm^2 areas were processed for the exposure duration of 120 s with the application of two different ion currents. The ion irradiation dose applied for 1 nA current was 3 x 10^{16} ions/ cm^2, while for 3 nA, an ion dose of 9x10^{16} ions/ cm^2 was used.

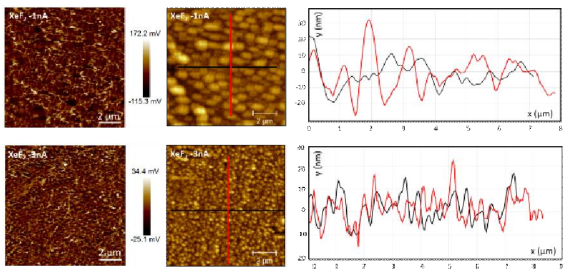

Fig. 8. QNM mode AFM adhesion maps, AFM topography images and corresponding surface profiles of XeF_2 assisted ion etched Melinex® foil surfaces treated using 1nA and 3nA ion beam currents.

The experimental work indicates that the use of XeF_2 for the gas assisted ion etching process leads to a dramatic change in the surface topography. As can be seen from the horizontal and vertical profiles, surface modification is in the range of nanometers. XeF_2 assisted ion etching results in an increase in the surface roughness values. It can be suggested that the gas molecules that penetrate through the polymer structure together with the ions tend to go out via forming new paths, resulting in an increase in the surface area. The decrease in the roughness values with increasing ion current is due to the amount of gallium ions that are implanted on the Melinex® and hence the smoothing of the surfaces by means of polymer softening.

Another series of gas enhanced etching on Melinex® was performed via electron beam irradiation this time using two different magnitude of beam current, e.g. 5 nA and 10 nA and varying exposure times. Fig. 9 and Fig. 10 show the QNM mode AFM topography images and corresponding adhesion maps of Melinex® foil surfaces after XeF_2 assisted e-beam exposure within 50x50 μm^2 square areas using 5 nA and 10 nA for increasing times and hence electron doses. According to the images, it can be suggested that there has been a significant morphology change occurred dependent on applied electron current.

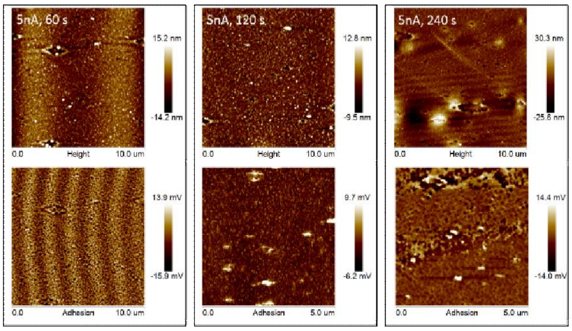

Fig. 9. QNM mode AFM topography images and corresponding adhesion maps of Melinex® foil surfaces after XeF_2 assisted e-beam exposure using 5 nA electron current.

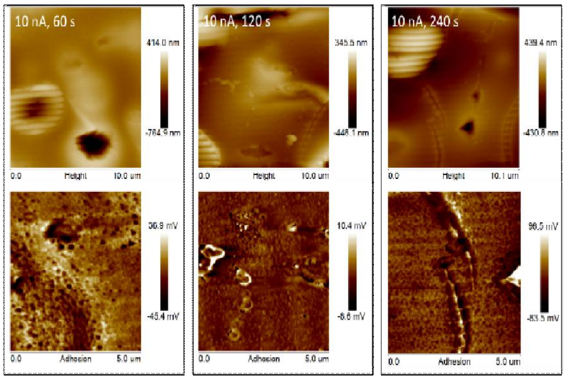

Fig.10. QNM mode AFM topography images and corresponding adhesion maps of Melinex® foil surfaces after XeF_2 assisted e-beam exposure using 10 nA electron current.

3.3. PP Samples

In Fig. 11, HR-SEM SE, AFM topography images and AFM surface profiles of bulk PP surfaces after ion etching are given. For this irradiation series, 30 keV ion energy and an ion beam current of 3nA was used for direct ion etching processes. 50x50 µm areas were processed for the exposure durations of 60s, 120s and 480s. There has been no significant variation in the surface texture towards increasing ion doses however there is a slight trend of surface smoothening and flattening due to the increasing amount of Ga^+ implantation.

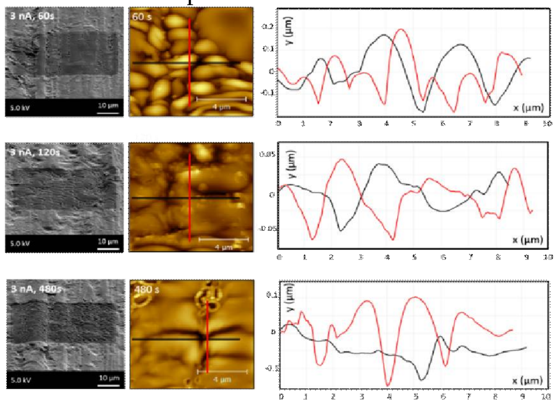

Fig.11. HR-SEM SE, AFM topography images and AFM surface profiles of bulk PP surfaces after ion etching using 3 nA ion beam current.

Fig. 12 shows HR-SEM SE, AFM topography images and AFM surface profiles of bulk PP surfaces after ion XeF_2 assisted ion beam etching. In energy of 30 keV and an ion beam current of 3nA was used for GAE processes within 50x50 µm areas for the exposure durations of 60s, 120s and 480s. XeF_2 assisted ion etching led to an increase in the depth profile as well as the formation of nano-hills with longer exposure times when compared to the direct ion etching series. This might be corresponded to the introduction of the gas molecules into the polymer structure during ion etching and escaping of the gas molecules away from the surfaces leaving behind characteristic textures.

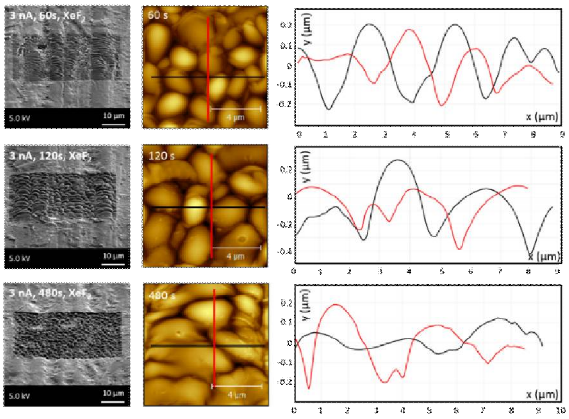

Fig. 12. HR-SEM SE, AFM topography images and AFM surface profiles of bulk PP surfaces after ion XeF_2 assisted ion beam etching using 3 nA ion beam current.

CONCLUSIONS

This work concerns the investigation of ion and electron beam based modification of three different polymers for controllable functionalization and nanostrcuturing of sample surfaces. For this work were high density polyethylene (HDPE), Melinex® and polypropylene (PP). For all polymer samples, direct and XeF_2 assisted gallium ion etching experiments were carried out using different instrumental parameters and processing conditions, which result in considerable variations in surface morphologies. This can be attributed to the differences in the behavior of surface adhesion properties of fluorine atoms that are adsorbed on the sample surfaces. Depending on the polymer type, different surface textures were observed for similar instrumental parameters and processing conditions in case of both direct and gas assisted etching experiments. When pristine surfaces are compared, among all three polymers, HDPE had the most actively modified surfaces by the application of same processing conditions

In addition, XeF_2 assisted electron beam irradiation experiments were performed for Melinex® samples for a direct comparison of the use of electron and ion beams for observing the alterations in nanostructuring. Unlike ions, a significant morphology change was observed with a variation on the applied electron current in case of gas assisted electron beam irradiation.

In conclusion, this work shows the availability and versatility of FIB-SEM dual-beam platforms for the application of nanomodification and nanostructuring processes on polymeric samples by means of maskless and direct lithography techniques. This, hereby, allows obtaining novel materials with functionalized surfaces having different adhesion and adherence characteristics, which then can be employed for different applications of science and technology.

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