MORPHOLOGICAL CHANGES OF ELECTRON-BEAM IRRADIATED PMMA SURFACE *

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Abstract

Atomic Force Microscopy (AFM) study of low energy (10keV) electron beam irradiated Polymethylmethacrylate (PMMA) surface was performed. PMMA thin film of (20 μm), were used in lithography technique. AFM in tapping mode has been utilized to investigate the morphological changes on the surfaces of sample as a function of fluence. TM-AFM showed the hills of the nano size surrounded by crater type features in all irradiated samples. The Root-Mean-Square (rms) surface roughness of the samples changed from 2.666 nm to 5.617 nm with fluence from $2x10^{14}e/cm^2$ to $1x10^{16}e/cm^2$. It shows that roughness increases with fluence.

INTRODUCTION

The surface properties of materials are usually different from those of the bulk because the surface atoms and molecules experience a different environment compared to those in the bulk. AFM has been a useful technique for acquiring topological information about surfaces. Recently, with the development of the tapping mode AFM (TM-AFM), both height and phase images can be obtained at the same time [1]. The primary interaction in the irradiation process is that of electron/electron collision and this results in large angle multiple scattering of the electron beam leading to the classic "Pear shaped" ionization volume around the point of entry into the material [2]. A dramatic improvement in the crosslinking response was observed for the decadiene polymer and consequently smaller electron beam irradiation doses were needed to obtain a certain degree to crosslinking [3]. The molecular weight and contact angle of water decrease with increasing dose of polymer film by electron beam irradiation. It shows wave like morphology also [4]. With N_2 ion implantation by the PIII(Plasma Immersion Ion Implantation) treatment, polymer surface became smoother and uniform except for some blisters scattered in the surface [5]. By AFM technique it has been shown that the ion implantation increase the amorphous phase content and decrease the crystallinity up to 70% from the original sample [6]. PMMA has been used widely as a positive working resist in electron beam lithography, and so the solubility of this polymer in organic solvents increases upon exposure to electron beam irradiation [7]. In the present study, AFM has been used to study the surface morphological effect on the PMMA irradiated with various fluences of electron beam at 10 keV.

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EXPERIMENTAL DETAILS

The PMMA film of thickness 20 μm and density 1.2 g/cm^3 was prepared by solution cast method. Figure 1 shows the repeating structural units of the PMMA polymer. The details of solution cast method have been given elsewhere [8]. The polymer sample was irradiated by 10 keV electron beam accelerator in high vacuum. The sketch diagram of the accelerator is shown in Fig 2. Detail of apparatus is given elsewhere [9]. 50 keV electrons beam penetrate up to depth of 40 μm in PMMA film, with a 20μm spread [2]. The current density was set up to 100 nm/cm^2 for irradiation. These samples were irradiated by 10keV electron beam with fluence of $2x10^{14}$, $4x10^{15}$ and $1x10^{16}e/cm^2$ at room temperature by electron accelerator. Atomic force microscopy is a powerful tool to characterize polymer film surfaces, as no special sample preparation is needed. In this study, electron irradiated and pristine PMMA surfaces have been structurally characterized by AFM using Scanning probe microscope from Digital Instrument USA with Nanoscope IV controller. The tapping mode was employed in air at the cantilever's resonant frequency (1-5 kHz) using a probe and cantilever unit composed of silicon tip with a tip radius of 20nm. Scans were made on different area selected on the film surface with fluence variation.

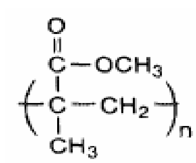

Figure 1:The repeating structural units of the PMMA polymer

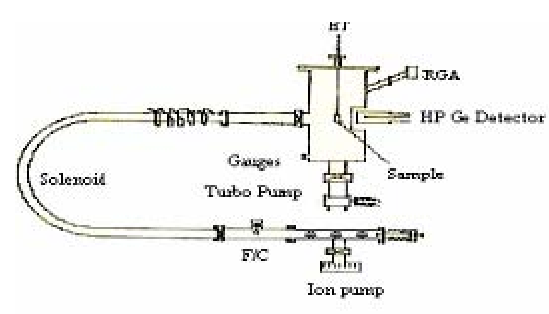

Figure 2: The sketch diagram of linear electron beam accelerator

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Table1: Mean square roughness and dimension measurements

Fluence (e/cm^2)	Roughness (nm)	Dimensions of the hills (nm)	
		Height	Diameter
Pristine	2.020	800	1000
$2X10^{14}$	2.666	10	200
$4X10^{15}$	2.941	30	500
$1X10^{16}$	5.617	5	200

RESULTS AND DISCUSSION

Atomic force microscopy was performed to examine the surface morphology and to measure roughness values for pristine and irradiated fluences with $2x10^{14}$, $4x10^{15}$ and 1 x $10^{16}e/cm^2$ PMMA samples. Figure3 and Figure4 show two and three dimensional topographic scan of the samples respectively. Results reveal that electron irradiated surface was rougher compared to the pristine sample surface. After irradiation the polymer film shows a remarkable change in yellow mounds with diameter from 1000-200 nm and topography (height) up to 5 nm. Results also shows large amount of pits of the order of 2.5nm-25 nm depth. The variation of rms roughness and dimension of the hills (average height and diameter) with fluence, measured from the manufacturer's software available with the microscope, are given in Table1. It can be seen from Table1 that the rms roughness for irradiated PMMA surface increases from 2.666 nm to 5.617 nm as its fluence increase from $4X10^{14}$ e/cm^2 to$1x10^{16}e/cm^2$. The increase in the roughness is due to the change in crosslinking density and degradation of a polymer surface. This result is consistent with other published works that report that surface confined polymerization can significantly change surface morphology and smoother rough surfaces [10]. Low energy He/Ar ions induced changes in polymer surface morphology are reported, that degree of modification can be clearly related to the ion type or energy [11].

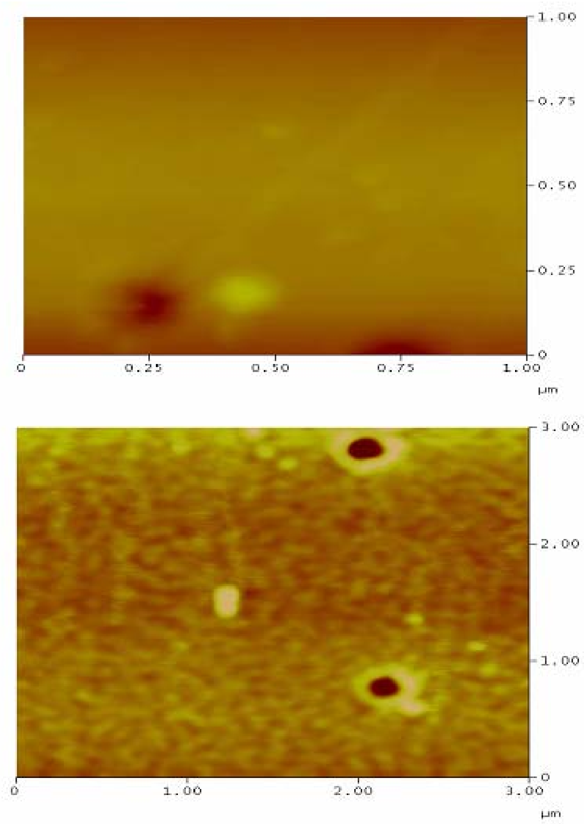

Figure 3: Two dimensional view of AFM micrograph of PMMA surface with 10 keV electron beam (a) Pristine and (b) irradiated at fluence $1X10^{16}$ e/cm^2

CONCLUSION

We conclude that the effect of electron beam irradiation on polymeric film results in the changes of surface morphology up to a few nanometers. The roughness of the sample increases with the fluence increase of the irradiation.

ACKNOWLEDGEMENT

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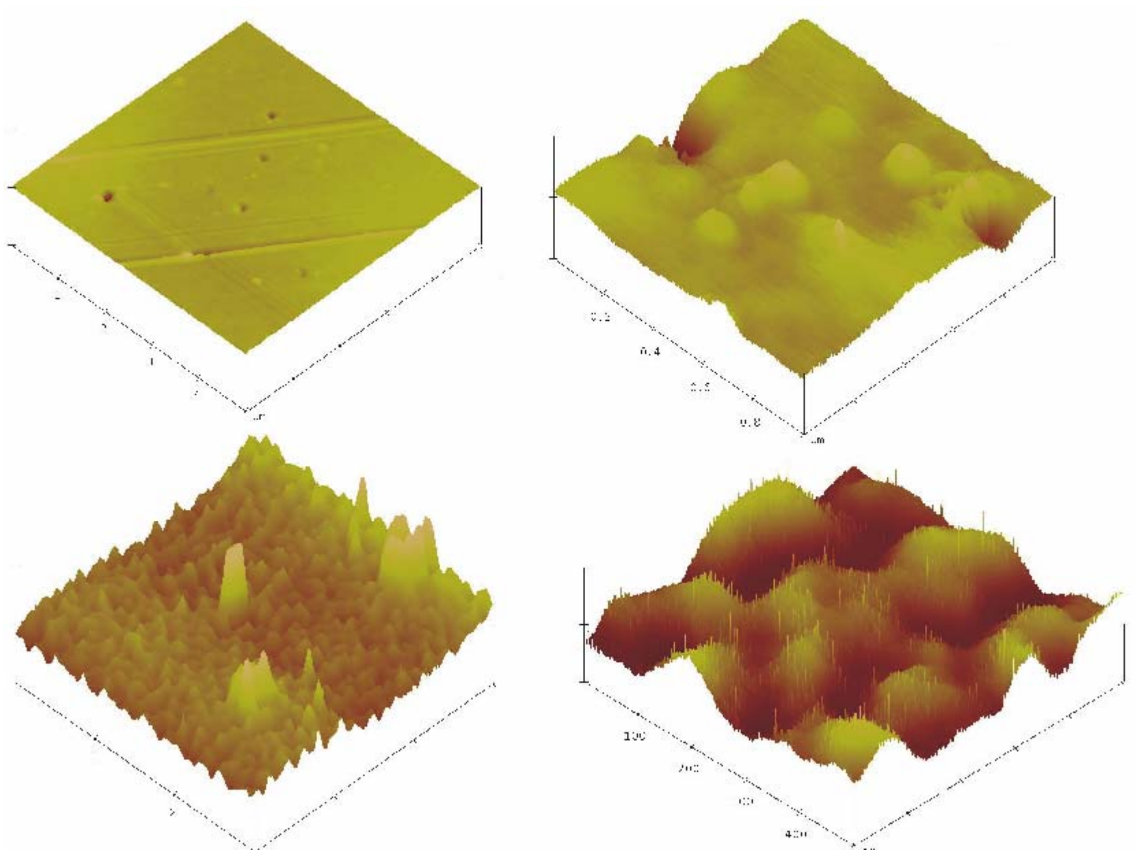
(a) (b)



(c) (d)

Figure 4: AFM images of (a) Pristine PMMA, (b) irradiated with fluence $4X10^{14}$ e/cm^2, (c) at fluence $4X10^{15}$ e/cm^2 and (d) at fluenec $1X10^{16}$ e/cm^2

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