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A Versatile Approach for Biomaterial Patterning: Masked Ion Beam Lithography

Kenneth E. Gonsalves[1*], Wei He[2], David B. Poker[3], Nikola Batina[4], Lhadi Merhari[5]
[1*]Department of Chemistry & C.C. Cameron Applied Research Center, University of North Carolina, Charlotte, NC 28223, [2]Institute of Material Science, U-136, University of Connecticut, Storrs, CT 06269, [3]Oak Ridge National Laboratory, Oak Ridge, TN 37831, [4]Departmento de Quimica, Universidad Autonoma Metropolitana-Iztapalapa, 09340 Mexico D.F., Mexico, [5]CERAMEC R&D, F-87000, Limoges, France

ABSTRACT

We describe a new approach for biomaterial patterning, viz, masked ion beam lithography. Poly (methyl methacrylate) (PMMA) film was used as a model system and subjected to Ca^+ and P^+ ion implantations through masks. Ca^+ ion implantation was performed at an energy of 85 keV with a fluence of $1x10^{14}$ ions/cm^2. P^+ ion implantation was done at an energy of 85 keV with fluences of $1x10^{15}$ and $1x10^{16}$ ions/cm^2. Arrays of holes were generated during these processes. AFM showed that the depth of the holes is in the nanoscale region. The surface hydrophobicity of the exposed PMMA films was investigated by contact angle measurement. The results indicated that ion implantation changed the surface hydrophobicity.

INTRODUCTION

Microfabrication technology, widely used in the microelectronics industry, has recently been applied in micropatterning biological materials ("biopatterning") [1]. Biopatterning has become increasingly important for the development of molecular and cellular biosensors, biomaterials, genomic and proteomic arrays [2]. In most cases photolithography is used. Although it is a quite mature technique, there are still some limitations in its application in biopatterning: (a) standard photolithography has multiple steps including film casting, exposure, developing and etching; (b) only the topography can be modified leaving a limited possibility to specifically tailor the surface chemistry of the patterns. In order to avoid the above shortcomings, we proposed to use ion implantation for the microfabrication process. Ion implantation is an important technique for implanting "dopants" in the manufacturing process of semiconductors. It is also a useful technique for improving surface properties of metals, such as wear and corrosion resistance [3]. In recent years, ion implantation has also been applied to modify polymer surfaces in order to improve tissue compatibility and blood compatibility [4]. The process is based on direct fabrication of patterns on polymers by ion irradiation. The fundamental underlying phenomena taken advantage of are the ion-polymer interactions. Indeed, compared to UV, X-ray or electrons, 1-400 keV ions lose a considerable amount of energy in the polymer leading to a thickness shrinkage of the exposed areas, thus inducing patterns of the desired shapes [5]. It is worth noting that no further treatment of the polymer is needed to reveal the features. The potential advantages of using ion implantation as a microfabrication techniques are: (a) since it is a one-step process, the patterns can be "machined" into the material in a controlled manner through masks; (b) by selecting the right ion to implant, such as Ca or P, the surface chemistry of the biocompatible material can be tailored, which may influence certain biological processes. In our study, the surface topography of poly (methyl methacrylate) PMMA film was modified by masked ion implantation, specifically, by Ca^+ ions and P^+ ions, leading to well defined microwells for potential bioMEM type devices.

EXPERIMENTAL DETAILS

Commercial poly (methyl methacrylate), PMMA, (M_w = 495K) was spin casted onto a 1" hexamethyl disilazane (HMDS) primed silicon wafer from a solution (4% in weight) in anisole at a speed of 1800 rpm for 60 s. The film was then baked at a temperature of 130 °C for 60 s. The thickness of the film was about 217 nm measured by Tencor Alphastep 200 surface profilometers.

A fine nickel mesh from Buckbee-Mears St. Paul, MN served as a mask, with a maximum transmittance of 36% and a 7.62 µm space between the wires. A piece of 0.7" x 0.7" mesh was placed on the PMMA film using copper tape. Implantation was then performed on an Extrion implant accelerator, a general purpose Cockcroft-Walton-type ion implanter with a modified Freeman source, in the Surface Modification and Characterization Research Center (SMCRC) at Oak Ridge National Laboratory. The implantations were performed by raster scanning the ion beam over a circular area of about 4 cm^2 area. Three different ion bombardment conditions were selected (all with 85 keV energy): 1) Ca^+ ion implantation with a fluence of $1x10^{14}$ ions/cm^2, 2) P^+ ion implantation with a fluence of $1x10^{15}$ ions/cm^2, 3) P^+ ion implantation with a fluence of $1x10^{16}$ ions/cm^2. The mesh was removed after the exposure, and the PMMA film was characterized using optical microscopy (Nikon EFD-3, Japan) equipped with a high performance CCD camera and atomic force microscopy (AFM) (Nanoscope III, DI). The hydrophobicity of the samples was investigated by performing contact angle measurement (NRL contact angle goniometer, NJ).

RESULTS AND DISCUSSION

A schematic illustration of the patterning process is given in Figure 1. The patterns on the

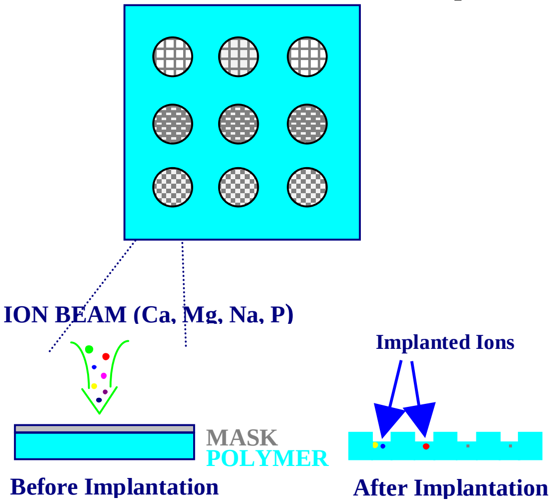


Figure1. Schematic illustration of the masked ion implantation process

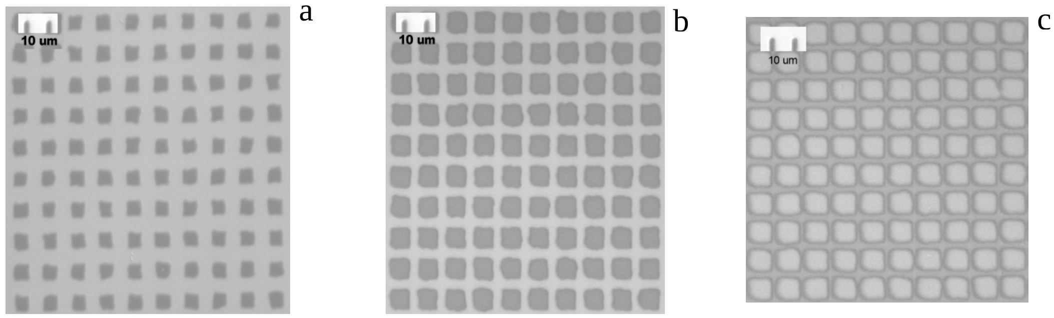


Figure 2. Optical microscopic results of samples irradiated with (a) 85 keV, 1x10^{14} ions/cm^2 Ca^+ ions; (b) 85 keV, 1x10^{15} ions/cm^2 P^+ ions; (c) 85 keV, 1x10^{16} ions/cm^2 P^+ ions.

samples can be described as orderly distributed square wells, as seen in the optical microscopy results (Figure 2). The images were obtained under 20 X magnifications. The scale bar represents 10 μm. The wells are formed as a result of the ion irradiation of the PMMA film under the open area of the mask. Thus the pattern on the mask was replicated onto the sample.

To further quantitatively characterize the patterns, an AFM was used to determine the surface morphology properties. Imaging was performed under laboratory atmosphere conditions, operating the AFM in the "tapping" mode [6]. It provided less contact between the AFM tip and the imaged sample, which leaves the sample surface in its intact state. Due to the same reason, images were collected with very slow scan rate of 1 Hz. Standard silicon probes (TESP) tips 125 μm long with typical frequency between 294 and 375 kHz were used. Images presented in Figure 3 and Figure 4 show 3-D sample topography with ordered patterns of very defined shape, which are distributed uniformly over the image area. In such topographic types of images, the upper part of the surface is always presented by lighter color. The observed patterns were characterized in great detail by determination of the surface roughness, shape and distributions of surface profiles. The AFM results of cross sections analysis (Figure 3) on the Ca^+ ions (85 keV, 1x10^{14}

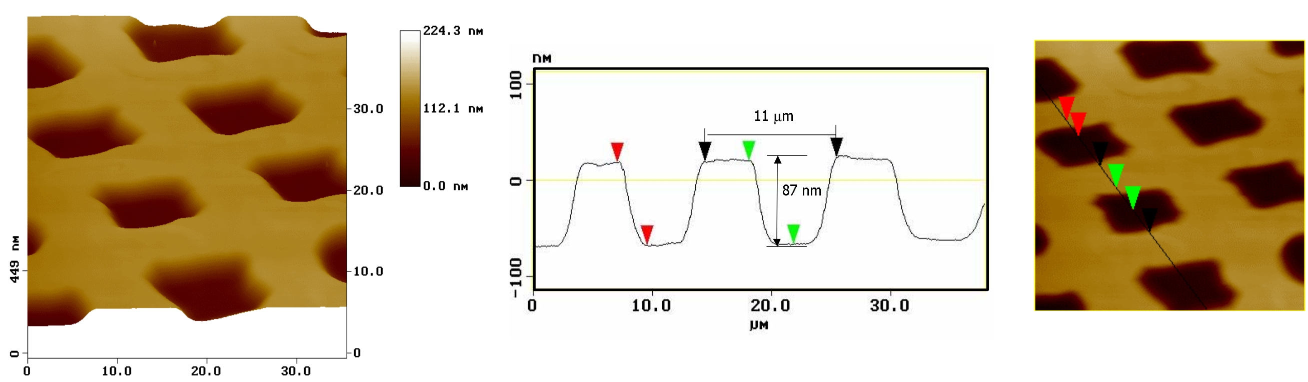
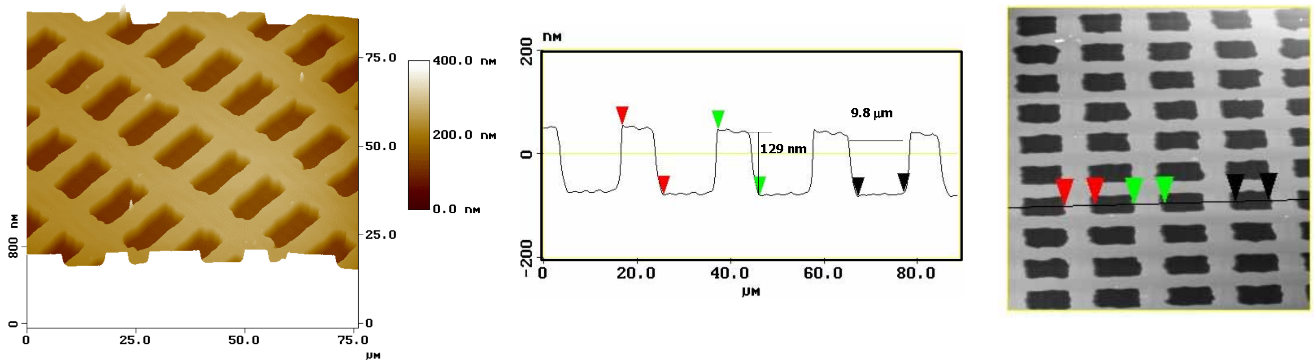
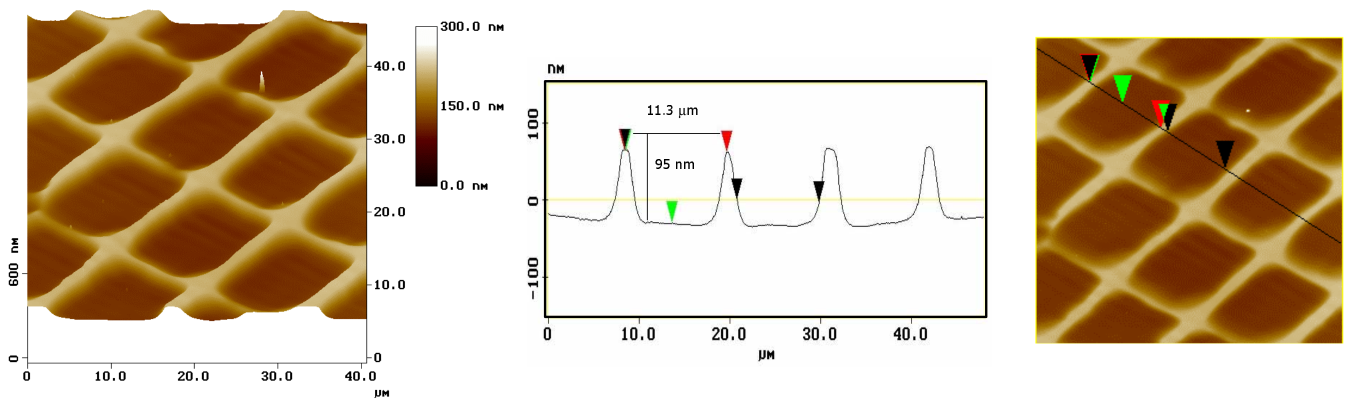


Figure 3. AFM images of the PMMA film surfaces irradiated with 85 keV, 1x10^{14} ions/cm^2 Ca^+ ions, recorded in the tapping mode with typical surface features characterized by a cross section analysis.



(a) 85 keV, 1x10^{15} ions/cm^2 P^+ ions



(b) 85 keV, 1x10^{16} ions/cm^2 P^+ ions

Figure 4. AFM images of the PMMA film surfaces irradiated with P+ ions, recorded in the tapping mode with typical surface features characterized by a cross section analysis.

ions/cm^2) irradiated sample showed that the distance between two isolated islands is about 11 µm, and the height of each island is about 87 nm. In Figure 4a, it shows a width of 9.8 µm, and a depth of 129 nm for P^+ ions (85 keV, 1x10^{15} ions/cm^2). In Figure 4b, where the exposure condition is P^+, 85 keV and 1x10^{16} ions/cm^2, the feature is 11.3 µm wide and 95 nm deep.

The hydrophobicity of the samples was investigated at room temperature by measuring the contact angle of distilled water dropped on the surface of the masked region using a NRL contact angle goniometer. The results are illustrated in Figure 5. Each value is an average over three measurements ($\pm$2°). It is seen that, compared with regular PMMA film, irradiation of the samples with Ca^+ ions at 1x10^{14} ions/cm^2 and P^+ ions at 1x10^{15} ions/cm^2 did not change the contact angle significantly. However, when the fluence of P^+ ions was increased to 1x10^{16} ions/cm^2, the contact angle increased to a higher value, 71.0° as compared to 61.7° for the regular PMMA. The higher contact angle indicates a more hydrophobic surface. It is known that surface hydrophobicity is related with the polarity of the surface. The less polar the surface is, the more hydrophobic it is. Indeed one of the effects of ion beam irradiation has been shown to be the removal of the surface oxygen functionalities, in this case, the loss of the methacrylate

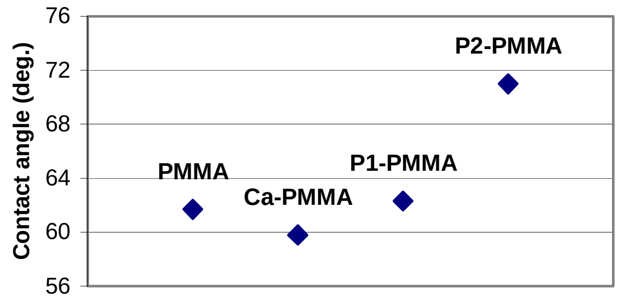


Figure 5. Contact angles of regular PMMA, and samples irradiated with 85 keV, $1x10^{14}$ ions/cm^2 Ca^+ ions (Ca-PMMA), $1x10^{15}$ ions/cm^2 P^+ ions (P1-PMMA), $1x10^{16}$ ions/cm^2 P^+ ions (P2-PMMA).

pendant group. As a result, the surface polarity is decreased leading to a more hydrophobic surface. IR study on the ion exposed PMMA film is currently underway to explore related chemistry during the exposure process. Osteoblast cells will also be cultured on these samples, cell adhesion, morphology as well as cell proliferation will be studied.

CONCLUSIONS

In summary, Masked Ion Beam technique has been tested as a versatile approach for biomaterial patterning using a PMMA film as the model. The results showed that not only the topography of the substrate can be changed, but also the surface chemistry can be tailored by implanting Ca/P ions. Surface hydrophobicity is also changed as a result of the ion bombardment. This will be a promising technique for biomaterial fabrication. The effects of the pattern geometry and implanted ion species on the growth of certain types of cells are currently being further investigated and will be reported subsequently.

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