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An angled nano-tunnel fabricated on poly(methyl methacrylate) by a focused ion beam

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Abstract
Angled nano-scale tunnels with high aspect ratio were fabricated on poly(methyl methacrylate) (PMMA) using a focused ion beam (FIB). The fabrication parameters such as ion fluence, incidence angle, and acceleration voltage of the Ga\(^{+}\) ion beam were first studied on the PMMA surface to explore the formation of the nano-scale configurations such as nano-holes and cones with diameter in the range of 50–150 nm at an ion beam acceleration voltage of 5–20 kV. It was also found that the PMMA surface exposed to FIB was changed into an amorphous graphitic structure. Angled nano-scale tunnels were fabricated with high aspect ratio of 700–1500 nm in depth and 60 nm in mean diameter at an ion beam acceleration voltage of 5 kV and under a specific ion beam current. The angle of the nano-tunnels was found to follow the incident angle of the ion beam tilted from 0° to 85°, which has the potential for creating a mold for anisotropic adhesives by mimicking the hairs on a gecko’s feet.

1. Introduction
Over the last few years, several techniques for surface modification of polymer surfaces have been developed, including plasma treatments, vacuum ultraviolet light or ion beam irradiation to improve wettability, adhesive properties and biocompatibility [1–4]. Among these techniques, a focused ion beam (FIB) is considered to be a well designed tool for fabricating micro- or nano-scale structures, particularly for the fabrication of localized and precise patterns, such as nano-fluidic channels and micro-lenses in precise control [1, 5, 6]. On relatively soft polymers, such as poly(dimethylsiloxane) (PDMS), with a compliant elastic modulus range of 1–10 MPa, it has been reported that FIB irradiation can be used to create ordered wrinkle patterns on the nano-scale with the evolution of a skin layer with high hardness and high compressive stress [1, 7]. The flexibility afforded by this technique was further studied to fabricate micro- or nano-scale structural features on soft polymers by controlling the ion energy and ion fluence [7–9]. However, it was reported that poly(methyl methacrylate) (PMMA), as a relatively harder polymer, could form several morphologies on the nano-scale, such as holes, cones or bubbles, under a variety of ion beam irradiation conditions, since it undergoes bond scission under a range of ion energies as well as ion fluences.

This study further explored the evolution conditions for the surface morphology on PMMA affected by FIB at various accelerating voltages, ion fluence and incident angles of the ion beam to construct a morphology map. High resolution transmission electron microscopy (HRTEM) and Raman spectroscopy were used to examine the surface characteristics altered by ion irradiation, revealing nanostructures with amorphous carbonization. An angled nano-tunnel array with high aspect ratio along the depth direction was fabricated by controlling the ion energy and incident angle of the ion beam, 0°–85°.
2. Experimental details

Commercially available PMMA, as a light guide plate in TFT-LCDs (LG MMA, HP202, South Korea), with a tensile strength of 720 kg cm$^{-2}$ (ASTM D638) and a density of 1.18 g cm$^{-3}$ (ASTM D792) at room temperature, was cut into pieces of 10 $\times$ 10 $\times$ 2 mm$^3$ for ion beam irradiation. Prior to ion beam irradiation, all pieces were cleaned thoroughly with methanol and triply deionized water to remove any surface contamination, and dried with a N$_2$ gas blower. To prevent the PMMA surface from electron and ion charging, a 20 nm thick Au layer was pre-coated using an ion-sputter coater (Eiko IB-3, Japan) with Ar plasma. Note that the ion beam induced morphologies of the Au-coated and uncoated PMMA surfaces were almost identical. The system for ion beam irradiation consisted of a FE-SEM/FIB dual-beam system (NOVA 200; FEI, Hillsboro, OR) equipped with a Ga$^+$ liquid metal ion source. A PMMA piece at a working pressure of 1.46 $\times$ 10$^{-5}$ Pa was exposed to Ga$^+$ FIB with acceleration voltages of 5, 10, 20 and 30 kV and ion currents ranging 0.15 pA–20 nA for a duration of 1 s to 10 min. The incident angle, defined as the angle between the incoming beam and the surface normal, was changed from 0$^\circ$ to 85$^\circ$ for angled nano-tunnel configuration. The dwell time of the ion beam was kept to 1 $\mu$s in digital raster mode on the PMMA surface with 20 $\times$ 20 $\mu$m$^2$. Images of the Ga$^+$ ion beam irradiated area were acquired using FE-SEM pre-installed in the FIB system.

The bonding structures of the surfaces before and after ion beam irradiation were characterized by a Jobin-Yvon Raman spectroscope (LabRam HR, France) under $\times 50$ objectives with excitation from the 514.532 nm line of an Ar laser at a power incident on the samples of 0.5 mW and a total accumulation time 100 s for each spectrum. The cross-sectional microstructure (prepared with the FIB system) of the polymeric substrate near the surfaces was examined by HRTEM (JEM-3000F, JEOL, Japan). The chemical composition of the surface layer at different depths was analyzed by energy dispersive x-ray spectroscopy (EDS, Oxford Instruments) equipped with an HRTEM system.

3. Results and discussion

Figure 1 shows the representative morphologies created by FIB irradiation according to the ion fluence and accelerating voltage. By selecting the formation of nano-scale tunnels on PMMA, figures 1(a)–(c) display how the ion fluence affects the configuration of the nano-tunnel at an incident angle of 0$^\circ$ with a diameter ranging from approximately 40 to 80 nm at a specific ion beam current (1.4 nA) and accelerating voltage of 5 kV. With increasing ion fluence, a sputter erosion phenomenon and ion beam induced void formation process occurred on the PMMA surface, leading to a thinner wall partition. Nano-holes (figure 1(d)) with diameters ranging from 50 to 150 nm were produced under a low acceleration voltage (5 and 10 kV) and ion fluence $<$ 2.1 $\times$ 10$^{17}$ ions cm$^{-2}$, while narrow cones (figure 1(e)) were observed at ion fluence $>$ 2.1 $\times$ 10$^{17}$ ions cm$^{-2}$. Nano-tunnels appeared at a narrow ion fluence range of approximately 0.4–1.8 $\times$ 10$^{17}$ ions cm$^{-2}$ and an accelerating voltage of 5 kV. Bubbles were induced at an acceleration voltage of 20, 30 kV and an wide range of ion fluences ($10^{15}$–$10^{18}$ ions cm$^{-2}$) on the PMMA surface ranging in sizing from 2 $\mu$m to more than 10 $\mu$m, as shown in figure 1(f). These morphologies were induced from sputtering phenomena and degradation occurring during irradiation, leading to considerable chain scission and fragmentation of the PMMA in a shallow subsurface layer. Figure 1(g) shows a morphology map of the PMMA surface at different acceleration voltages and ion fluences. A specific morphology appears in a certain range of beam conditions.

Four characteristic morphologies (nano-hole, nano-tunnel, narrow cone, bubble) on PMMA were reported to form with two main mechanisms [10–15]. Firstly, PMMA is degraded with the bond scission by the bombardment of the energetic ions in a variety of irradiation condition. When the ion irradiation starts, the surface of PMMA was quickly modified into the graphitic structure, which would decrease the penetration of Ga ions into the deeper subsurface layer. The etching happens not only from the PMMA surface but also beneath it. As a result, simple gaseous molecular species, such as CO, CO$_2$, HCOOCH$_3$, CH$_4$ and H$_2$, are released [10–12]. The formation of such volatile species is clearly associated with the degradation of the ester pendent group of PMMA (–COOCH$_3$) [10–12]. Simultaneously, the volatile fragments that are not released from the surface can form gaseous bubbles if their concentration exceeds their solubility in PMMA. Below the PMMA surface, gaseous molecular species released by ion energy would push up the surface layer, then make a bubble configuration. Bubbles do not consist of Ga but gases from broken bonds of the original PMMA bond structure. These are produced by the radiation–chemical reactions in an affected subsurface layer with a thickness of the order of the ion penetration depth [10]. Therefore, bubbles can be generated if the low molecular weight fragments are formed faster than they are desorbed from the surface. The apparent gas formation within the surface layer appears to depend on the ion beam energy characteristics as well as the polymer nature such as gas yield, glass transition, melting point and melt viscosity [13].

However, in the second mechanism, nano-holes, narrow cones and the nano-tunnel are fabricated by ion beam induced void formation and a sputter erosion phenomenon under a relatively low beam energy of 5 or 10 kV. When PMMA is irradiated with Ga$^+$ ions, it can penetrate to the surface layer and create many vacancies or voids due to the formation of over-saturated vacancies in the subsurface [14]. In the case of this, the low molecular weight fragments are formed more slowly than they can be desorbed from the surface. So they are not released from the subsurface. Nano-holes are an initial configuration of modification under the low acceleration voltage using FIB. If the ion fluence increased further, the nano-holes were changed to the configuration of narrow cones by sputter phenomena. The corners of the partitioning wall (wall of the hole) are gradually sputtered away to form slopes at a stable gradient, which meet each other to form cones. The width and height of the cones decreases with increasing ion beam fluence and finally disappears [15, 16]. Furthermore, with the solubility exceeded the low molecular...
weight fragments at the subsurface layer would work as voids during the ion beam sputter process. If these voids were more densely distributed and aligned along the depth direction at the specific irradiation conditions of the ion beam, the nano-tunnel could be induced and be longer. It should be considered that the formation mechanism of the nano-tunnel would be a
specific condition from that of the nano-hole in terms of the void density at the subsurface layer.

The PMMA surfaces were characterized by Raman spectroscopy before and after Ga\(^+\) ion beam exposure in figure 2. Pristine PMMA was known as an amorphous polymer, while a graphite-like structure was observed as a result of a chemical reaction induced by ion beam irradiation in the affected region. The exposed surface of the PMMA sample showed new bands at approximately 1360 cm\(^{-1}\) and 1585 cm\(^{-1}\), which were assigned to the D peak for disordered bonding and the G peak for graphite, respectively, confirming the coexistence of an amorphous carbon line structure [17–19]. Furthermore, it can be expected that this newly formed graphitic layer would be more conductive than pristine PMMA, as indicated in the literature [20].

The depth profile of the irradiated PMMA was examined by HRTEM equipped with EDS in figure 3. Figure 3(a) shows the sampling position (yellow box) for TEM and EDS analysis. A nano-scale cone-type configuration was chosen at an accelerating voltage of 10 kV, an ion fluence of 2.625 \(\times\) 10\(^{18}\) ions cm\(^{-2}\) and an incident angle of 0°. Figure 3(b) displays a low magnification image of TEM, revealing that the profile of Ga ion penetration forms a new layer underneath the PMMA surface while the new layer corresponds to the incident angle [1]. Figure 3(c) shows the depth profile by EDS mapping indicating the distribution of Ga (from the ion beam source) and Pt (a post-deposition layer to protect the ion beam irradiated surface from damaging during TEM sampling) from the surface to the ion beam irradiation direction. The newly formed layer was composed of a Ga rich component doped into the PMMA surface within 30 nm of the surface and its thickness would depend on the accelerating voltage of the ion beam [5]. Therefore, Raman analysis and EDS line-scan confirmed that the chemical bond and composition of the newly formed layer had been altered by Ga\(^+\) ion implantation.

For further applications of the configuration of the nano-tunnel with a high aspect ratio and narrow shell thickness, the ion beam incident angle was varied from 0° to 85°, as shown in figure 4. At the fixed condition of a low acceleration voltage of 5 kV and ion fluence of approximately 10\(^{17}\) ions cm\(^{-2}\), the cylindrical nano-tunnel was tilted to follow the ion beam irradiation direction. The images of the left side in

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**Figure 2.** The Raman spectra of the PMMA sample surface. Variations in Raman shift of the pristine PMMA after ion beam exposure.

**Figure 3.** (a) SEM image of the sampling position (yellow box) for TEM analysis. The irradiation conditions are 10 kV acceleration voltage, 2.625 \(\times\) 10\(^{18}\) ions cm\(^{-2}\) ion fluence and 0° incident angle. (b) Low magnification image of TEM cross-section and (c) TEM cross-sectional image of the PMMA surface after ion irradiation and the depth profile of the chemical components obtained from the EDS line-scan.
Figure 4. (a)–(c) Plan view (left) and cross-section view (right) of SEM images of the nano-tunnel structure with an angled configuration and a high aspect ratio at various incident angles of (a) 0°, (b) 30° and (c) 60°, which were defined as ‘α’ by the ion incident direction (arrowed) and the surface normal of PMMA (dotted) on the right of (b). (d) Plan-view SEM images at two ion incident angles of (d) 70° and (e) 85°. The numbers for (a)–(e) are the ion fluences (ions cm\(^{-2}\)). The acceleration voltage of (a)–(e) is fixed at 5 kV. Scale bar for (a)–(e) = 500 nm.

figures 4(a)–(c) were taken after ion beam irradiation, and show the top-view and right side after cross-sectioning for the side-view at incident angles of 0°, 30° and 60°, respectively. In figures 4(b) and (c), the tunnels are slightly bent toward the surface, which can be induced by unexpected stress caused by the ion beam broadening effect. This might be understood from the literature finding that the ion beam bombardment on the solid surface would cause the deformation corresponding to the surface stress in compression [1, 21, 22]. As the side of the tunnel facing toward the ion beam might be exposed with
slightly more ion fluence than the other side of the tunnel, the surface stress in compression induced by the ion irradiation can be generated further on the facing side of the tunnel, which would make the tunnel bend toward the surface. An average diameter was measured at approximately 60 nm while the length of each tunnel ranged from 700 to 1500 nm with increasing incident angle due to the longer projected area of the Ga$^+$ ion beam for higher incident angles on the PMMA surface at a similar range of ion fluence. Surface etching was found to be dominant at incident angles of 70° and 85°, as shown in figures 4(d) and (e), respectively. The formation of a nano-pattern aligned along the ion beam projection direction with a uniform width appeared similar to the ripple formation on a PI or Si substrate induced by a focused ion beam [5, 23].

4. Conclusions

Nano-scale surface features on the PMMA surface were fabricated using a focused ion beam. The formation conditions for nano-scale holes, cones, bubbles and tunnels were examined at different accelerating voltages, ion fluences and incident angles. Raman and EDS line-scan exhibited that the PMMA surface exposed to FIB was changed into an amorphous graphitic-like structure at the top surface of the Ga implanted layer. Nano-tunnel-like configurations with an average diameter of approximately 60 nm and a depth of 700–1500 nm were produced at a certain ion beam fluence. The anisotropic or angled nano-tunnel-like structures were fabricated by tilting the incident angle of the ion beam, which can be exploited for mold applications to create anisotropic adhesives mimicking the hairs on a gecko’s feet.

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