

Combining a Fluoroalkylsiloxane and Ion Implantation for Hydrophilic/Hydrophobic Patterning

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ABSTRACT

We present a novel method of producing hydrophilic/hydrophobic patterning on several different substrates using a novel two-step process. The developed process involves a simple surface functionalization with a fluoroalkylsiloxane, followed by masked ion implantation. This method allows for the patterning of many different substrates, with only two facile steps, producing the same degree of hydrophilicity and hydrophobicity irrespective of the wettability of the initial substrate. This paper discusses applications of this process on polymer, metal and glass substrates.

Keywords: hydrophilic, hydrophobic, patterning, fluoroalkylsiloxane, ion implantation

1 INTRODUCTION

The way in which water interacts with surfaces has an impact on many different industries and so the ability to control this interaction and determine the wetting behavior of a surface allows for the development of intelligent interfaces to overcome challenges and improve efficiency in many areas. Compared to uniform surface properties, the design of a surface with particular areas of hydrophilicity and areas of hydrophobicity allows for a greater control of the wetting behavior and flow of water across the surface. This has well-known application in microfluidics [1]–[4], but can be of use in many different industries where benefits can be gained through controlling behaviors at the interface between water and a surface, such as heating and air conditioning [5],[6], and water harvesting [7],[8], in particular.

As there is a wide range of potential applications for hydrophilic/hydrophobic patterning, there is a similarly large variety of substrate materials that may be used in these applications, As some applications require other material characteristics, it is not always possible to utilize different materials to achieve hydrophilic/hydrophobic patterning, without producing a less efficient surface due to a loss in other properties. Hence, it is desirable to have a method of hydrophilic/hydrophobic patterning that can be applied to

different substrate materials, without significantly affecting the other physical properties of the surface.

Existing methods of hydrophilic/hydrophobic patterning generally utilize lithography/etching techniques and chemical vapor deposition (CVD) [9]–[12]. These methods involve numerous steps, many of which are often delicate and require many resources. These existing methods also often require specific substrates or rely on relatively thick surface coatings, which can alter other performance properties of the surface. Many existing methods, such as that used by Kobayashi *et al.* [12], utilize a hydrophilic substrate and areas of this substrate remain exposed in the final surface, providing the hydrophilic areas of the pattern. This inherently limits the process to substrate materials with relatively high inherent hydrophilicity, which is not always achievable when considering specific applications. Other methods, such as that used by Ishizaki *et al.* [11], use various methods of CVD to deposit a hydrophilic surface onto the substrate, followed by other processes to create the hydrophobic domains. However, these methods are also limited to substrate materials that are suitable for CVD processes.

Conversely, we have developed a novel system that allows facile hydrophilic/hydrophobic patterning of a surface with only a two-step process that can be applied to several different types of substrate material. Firstly, a facile surface functionalization is applied to the surface using a fluoroalkylsiloxane (FAS), to impart hydrophobicity to the surface. This step is then followed by an ion implantation treatment applied through a mask, to create areas of hydrophilicity. The FAS functionalization and ion implantation can be applied to a number of substrates and the resulting hydrophilicity and hydrophobicity is dependent on the chemistry of the FAS and products resulting from the ion implantation, hence this system can be applied to a number of different substrate materials, while achieving the same hydrophilic/hydrophobic pattern with similar wetting properties. As this process affects only the surface chemistry, any surface roughness present in the substrate will be retained and will affect the achieved degree of hydrophilicity/hydrophobicity.

This novel process is being developed on polymer, metal and glass substrates.

2 METHODS

2.1 Substrates and Preparation

Three types of substrates were utilized in these investigations, polymers, metals and glass. The polymers used were polyoxymethylene (POM), polymethylmethacrylate (PMMA), polycarbonate (PC), and polyvinylchloride (PVC). All samples were cut from polymer sheets. These polymers were chosen as they are commonly used in manufacturing. The metals used were aluminium (Al), steel (St) and stainless steel 316 (SS). Again all samples were cut from sheet metal. These metals were chosen as they are most commonly used in industry. Glass was also investigated, using glass microscopy slides.

Different types of substrate were chosen to demonstrate the applicability of this process to a range materials for different application, hence the materials chosen were materials commonly used in industrial applications. All substrates were cleaned before functionalization steps, with hot soapy water followed by ethanol.

2.2 FAS Functionalization

The FAS used in this process was Dynasytan F8815, a commercially available fluoroalkylsiloxane. This FAS was chosen as it is water-soluble, lending itself to facile processing. A solution of 2 wt% Dynasytan F8815 (FAS) was prepared in distilled water. Each substrate was submersed in 2 wt% FAS solution for 10 minutes. After this time had elapsed the functionalized substrate was removed from the solution and patted dry with paper towels. The samples were left to fully dry at room temperature.

2.3 Ion Implantation

After the FAS functionalization each sample was treated with ion implantation. The ion implantation treatment was applied to the samples with a mask. In these investigations the mask used simply covered half of each sample, to clearly demonstrate the effects of the process, however the shape of the mask has no effect on the treatment and so more complicated masks may be used. Samples were treated using Ar^+ ions with a fluence of greater than 10^{16} atoms cm^{-2} . The beam current density was kept low ($<3 \mu\text{A}$) to prevent significant heating of the samples.

2.4 Characterization

A custom-built goniometer was used to measure the apparent water contact angle (CA) of samples. The CA of each substrate was measured before FAS functionalization, after FAS functionalization and after masked ion implantation treatment. Apparent water contact angle measurements were taken by capturing a back-lit photo of 10 μL droplet of distilled water on the sample surface. The volume of the droplet was measured in a gas-tight syringe

and the droplet placed gently onto the surface from above, without the droplet free falling at any point to minimize impact on the surface. The image was then analyzed using the computer program ImageJ with a plug-in called Dropsnake to calculate the left and right CA values [13],[14]. Three droplets were analyzed per sample and three calculations were performed on each droplet, with the left and right CA averaged for each calculation. These nine values were then averaged and the mean taken to represent the final value, with the standard deviation calculated as the uncertainty.

3 DISCUSSION OF RESULTS

FAS functionalization is able to be carried out in aqueous solution as the FAS used, Dynasytan F8815, is water-soluble. This allows for a facile dip coating method, with only 10 minutes soaking required. The FAS functionalization was successful on all substrates and increased the CA of the samples to approximately 95-105°. The CA achieved after functionalization is dependent on the roughness and so varies slightly between samples. As these substrates were all generally flat, the CA of the FAS functionalized surfaces remained relatively low. However, it has been shown that this functionalization on rough substrates can achieve CA values of over 120°, dependent on the roughness pattern of the surface [15].

With a hydrophobic surface established after the FAS functionalization, the ion implantation treatment is then applied to the surface through a mask, to disrupt the FAS and destroy the hydrophobicity in targeted areas. The ion implantation treatment used in this process has been optimized to provide the highest degree of hydrophilization and to ensure hydrophobic recovery of the polymer does not occur. After ion implantation the treated areas of the surface become hydrophilic with decreased CA values, again the exact CA values achieved varied, dependent on the surface roughness of the sample. All of the samples in this investigation were found to have CA values sufficiently decreased to be described as formally hydrophilic. Again, the actual CA values achieved were dependent on the roughness of the sample surface and, as shown previously [15], the hydrophilicity of the treated sample is increased with increased surface roughness.

Ion implantation is widely known to cause severe damage to organic polymers, however the specific chemical and physical processes that occur to cause this damage are not fully understood. It has been shown that chain scission and cross-linking occurs in the polymer at the surface, leading to increased conjugation of the polymer, towards a fully graphitized surface in extreme cases [16],[17]. This is known to lead to changes in the physical properties of the surface, including increased wettability [18]. However, ion implantation on fluoropolymers has not been investigated in the same manner. Hence, the chemical reactions that occur and mechanism of damage have not yet been investigated and remain unknown. In this investigation, ion implantation

was found to have similar effects on the FAS treated surfaces as expected from organic polymer substrates after ion implantation. A significant increase in wettability was induced and the surface was rendered hydrophilic. This indicates that the mechanisms occurring are potentially the same as those seen to occur in the ion implantation of organic polymers.

As the penetration depth of the ion implantation treatment used here is very shallow, masks can be made from many different substrates; even permanent marker provides a layer thick enough to protect the underlying substrate. Hence, this allows for many different methods of mask production to be used and opens the possibility of producing masks using specialized techniques providing very fine detail, or producing masks using more simple techniques, depending on the requirements of the final application of the surface.

4 CONCLUSIONS

This novel process of hydrophilic/hydrophobic patterning has been demonstrated on several different substrates, including polymers, metals and glass. The FAS functionalization successfully increases the CA of all substrates and can be increased to achieve greater CA values on substrates with higher degrees of surface roughness. The ion implantation treatment can easily be masked, to affect only the FAS-functionalized areas of the substrate exposed to the ion beam. This ion implantation process successfully hydrophilizes the targeted areas, creating the desired hydrophilic/hydrophobic patterning.

This novel process is comprised of only two facile steps and can be applied to many different substrates. This shows that the process can easily be used in many different industries for surfaces with different applications.

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REFERENCES

[1] Feng, Y.; Zhou, Z.; Ye, X.; Xiong, J. *Sensors Actuators, A Phys.* 108, 138–143, 2003.

[2] Trantidou, T.; Elani, Y.; Parsons, E.; Ces, O. *Microsystems Nanoeng.* 3, 16091, 2017.

[3] Sridharamurthy, S. S.; Jiang, H. *IEEE Sens. J.* 7, 1315–1316, 2007.

[4] O’Loughlin, M.; Priest, C.; Popescu, M. N.; Ralston, J. J. *Colloid Interface Sci.* 402, 259–266, 2013.

[5] Mahapatra, P. S.; Ghosh, A.; Ganguly, R.; Megaridis, C. M. *Int. J. Heat Mass Transf.* 92, 877–883, 2016.

[6] Mondal, B.; Mac Giolla Eain, M.; Xu, Q.; Egan, V.

M.; Punch, J.; Lyons, A. M. *ACS Appl. Mater. Interfaces* 7, 23575–23588, 2015.

[7] Zhai, L.; Berg, M. C.; Cebeci, F.; Kim, Y.; Milwid, J. M.; Rubner, M. F.; Cohen, R. E.; Fevzi, C. *Nano Lett.* 6, 1213–1217, 2006.

[8] Pastine, S. J.; Okawa, D.; Kessler, B.; Rolandi, M.; Llorente, M.; Zettl, A.; Frechet, J. M. J. *J. Am. Chem. Soc.* 130, 4238–4239, 2008.

[9] Tsougeni, K.; Papageorgiou, D.; Tserepi, A.; Gogolides, E. *Lab Chip* 10, 462–469, 2010.

[10] Bodas, D.; Khan-Malek, C. *Sensors Actuators, B Chem.* 128, 168–172, 2007.

[11] Ishizaki, T.; Saito, N.; Takai, O. *Langmuir* 26, 8147–8154, 2010.

[12] Kobayashi, T.; Shimizu, K.; Kaizuma, Y.; Konishi, S. *Lab Chip* 11, 639–644, 2011.

[13] Stalder, A. F.; Kulik, G.; Sage, D.; Barbieri, L.; Hoffmann, P. *Colloids Surfaces A Physicochem. Eng. Asp.* 286, 92–103, 2006.

[14] Stalder, A. F.; Melchior, T.; Müller, M.; Sage, D.; Blu, T.; Unser, M. *Colloids Surfaces A Physicochem. Eng. Asp.* 364, 72–81, 2010.

[15] Cook, M. J.; Johnston, J. H.; Leveneur, J. *Anisotropic Wetting Behaviour of Modified 3D Printed Micro-Structured Polymer Surfaces for Water Harvesting.* In *TechConnect Briefs*; 2017; Vol. 1, Advance, pp. 295–297.

[16] Dong, H.; Bell, T. *Surf. Coatings Technol.* 111, 29–40, 1999.

[17] Lee, E. H. *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* 151, 29–41, 1999.

[18] Kondyurin, A.; Bilek, M. *Interactions of Ion Beam with Polymer: Physical Picture.* In *Ion beam treatment of polymers: application aspects from medicine to space.*; Newnes, Ed.; 2008; pp. 1–10.