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PREPARATION AND CHARACTERIZATION OF ALKYL-THIOLS MONOLAYER ON GLASS SUBSTRATES BY MICROCONTACT PRINTING

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ABSTRACT

Surface modification is a fascinating method to tailor the surface of material properties such as hydrophilicity, roughness, surface charge and many more. The modification is not only limited to solid materials, but could be possibly extended to particular liquid surfaces. In this paper, surface modification of glass slides with self-assembled monolayers (SAMs) of (3-Mercaptopropyl) trimethoxysilane (MPTMS) was conducted by using a simple method of microcontact printing. Characterizations of the self-assembled monolayer were realized by 3 techniques; (1) Atomic Force Microscopy (AFM) to determine the height of self-assembled monolayer and obtain the topography image, (2) X-ray Photoelectron Spectroscopy (XPS) to further confirm the thiol groups were grafted on the surface and (3) Confocal Fluorescence Microscopy (CFM) to visualize the reaction between thiol terminal groups and fluorescent probe. From the experiment conducted, the result showed that the MPTMS was successfully stamped on glass substrates. AFM scanning images displayed the 0.8±0.2nm height of MPTMS, which matching the size of the MPTS molecules (0.7±0.05nm). XPS spectra indicated the appearance of the doublet structure in the S_{2p} region ($S_{2p3/2}$ and $S_{2p1/2}$ levels of the S energy levels) with two peaks in binding energy of 162.8 and 163.8eV respectively. CFM imaging indicated the fluorescent patterns on glass substrates.

Keywords: surface modification, self-assembled monolayers, microcontact printing.

INTRODUCTION

Self-assembled monolayers (SAMs) are molecular assemblies and ordered of organic molecules formed by spontaneously adsorption on a substrate surface [6]. In surface science, SAMs provide the ability to control over the surface modification at the molecular level [3]. Hence, SAMs have been used in many fields that related to surface modification like in anti-corrosion surface [5], control of surface wetting and dewetting [8] and control of bio-compatibility [10]. Furthermore, SAMs can also be prepared by using different types of molecules (both aliphatic and aromatic containing functional groups (such as -SH, -COOH, $-NH_2$) and substrates (glass, mica, Si, metal, gold) [2].

There are many techniques to prepare SAMs such as microcontact printing, ultraviolet (UV) lithography, electrodeposition, and chemical or physical vapor deposition. However, among those techniques, microcontact printing is widely used since it offers a low cost and simple surface patterning methodology up to sub-micrometer and nanometer in dimension [11]. In this method, there are 2 main steps; fabrication of polydimethylsiloxane (PDMS) stamps and printing on the substrate as illustrated in Figure-1 and Scheme 1. Basically, an elastomeric PDMS stamp is 'inked' with a precursor molecule of SAMs and then printed onto the substrate to produce SAMs on the stamped areas [9]. It is noted that only the areas that come into contact with stamps are covered with SAMs while unstamped areas remain bare. In [4] utilized microcontact printing in the preparation of Janus polymer microparticles with amino-β-galactoside and amino-mannoside under ambient conditions where the microparticles served as a substrate. Microcontact printing was also employed for the functionalization of glass beads with aminosilane monolayer and for the immobilization of different alkyne-modified carbohydrate on azide terminated monolayers, which can be applied for further protein (lectins) binding to the substrate surface [1].

In this paper, a facile method to graft self-assembled monolayer of trimethoxysilane (MPTMS) on glass substrates by using microcontact printing is described. After grafting of MPTMS onto substrate, the terminal of thiol groups were reacted with Fluorescein-5-maleimide diacetate. Atomic Force Microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and Confocal Fluorescence Microscopy (CFM) serve as main investigative tools for determination of thiol groups covalently attached on glass substrates.

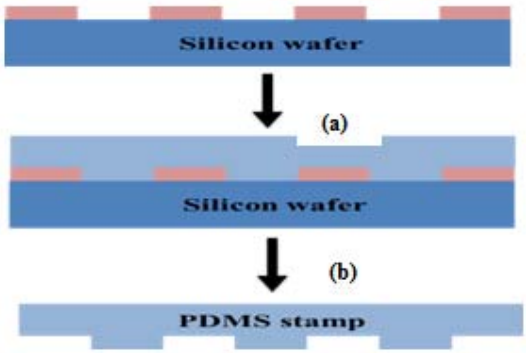


Figure-1. Preparation of PDMS stamp from the silicon wafer master. The silicon wafer was prepared with electron beam lithography containing desired patterns; (a) Prepolymer elastomer was poured onto the wafer, (b) After curing overnight in the oven, the PDMS was removed and peeled off.

MATERIALS AND METHODS

Materials

(3-Mercaptopropyl) trimethoxysilane (MPTMS) 95%, anhydrous toluene 99.8% and fluorescein-5-maleimide diacetate were purchased from Sigma-Aldrich and used as supplied. Sylgard-184 elastomer was obtained from Dow Corning. Glass substrates, 24 x 24mm and 18 x 18mm (microscopy cover slides) were delivered from VWR International. Silicon wafer containing micro patterns was purchased from Dow Corning Corporation and Kavli Nanolab, Delft University of Technology (TU Delft), the Netherlands. Surface cleaning procedures were carried out by using absolute ethanol and Milli-Q water.

Preparation of PDMS stamps

PDMS stamps were prepared by casting and curing the mixture of Sylgard 184 pre-polymer and curing agent against electron beam resist micro patterned silicon wafer which contained a negative image of the fabricated patterns. The master consists of different patterns such as dots, holes and lines in micrometer size. The PDMS stamps were cured at 60 °C for 12 hours. After 12 hours, the PDMS stamps were cut around the pattern area by using a scalpel (1cm x 1cm).

Substrate surface pretreatment

The glass substrates were treated in H_2SO_4 at 60ºC for 12 hours, and then rinsed with deionized H_2O and ethanol and dried under a nitrogen stream. Prior to microcontact printing, the glass substrates were treated in an oxygen plasma oven for 3 minutes in order to introduce silanol groups on the substrate surface.

Microcontact printing of Thiols on substrate

An inking solution contains 20% v/v of MPTMS in anhydrous toluene was prepared. About 50µl of inking solution was dropped on a microscope slide, and then a PDMS stamp was placed on top of the inking solution for 15s. Next, the stamp was dried in air for 1 min followed by dried under a nitrogen stream until excess solvent removed. The inked stamp then was dropped on the treated glass at 60 °C for 2 minutes. After that, the glass substrate was heated with heat gun at 200 °C for 1 min.

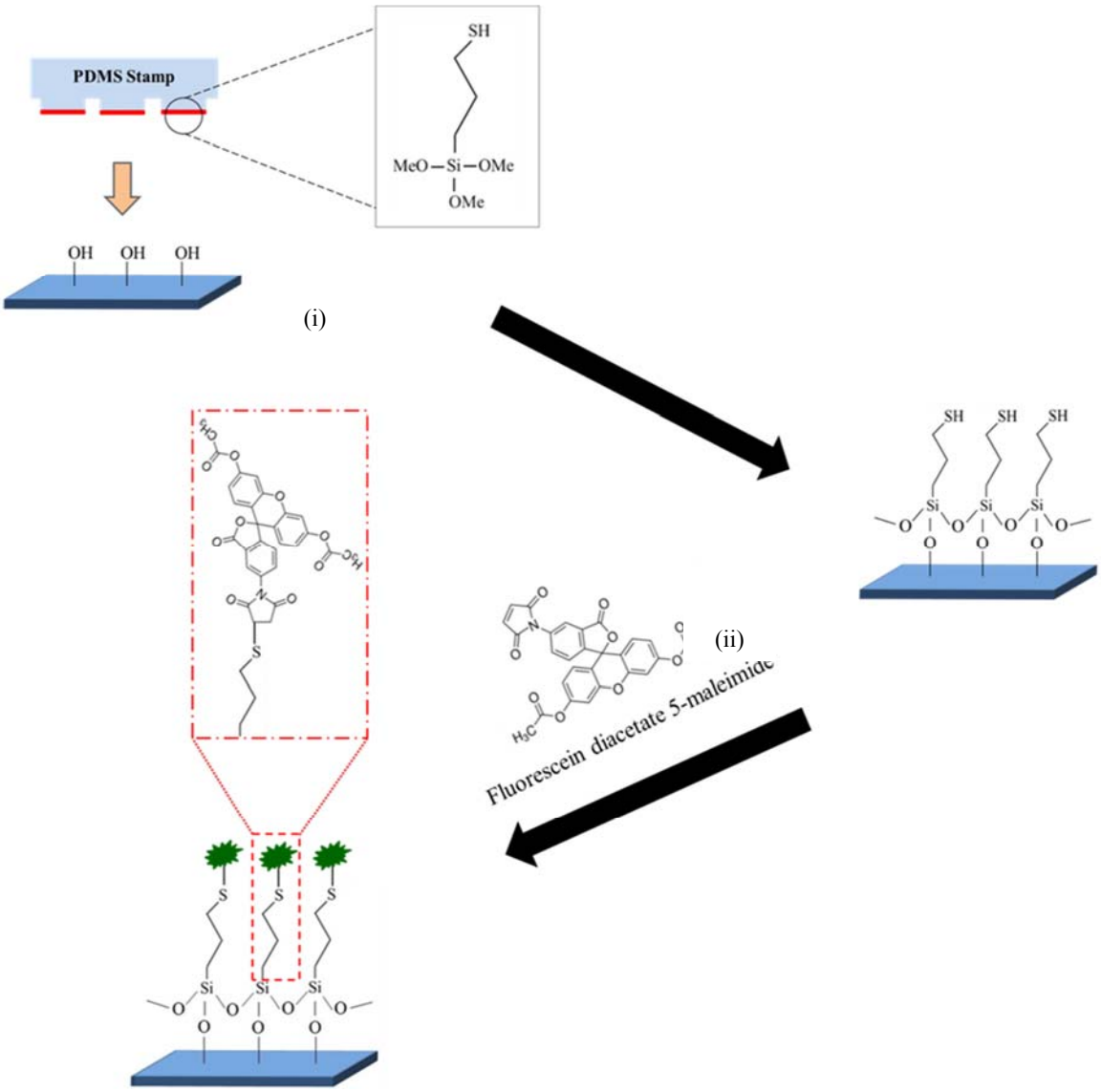
Functionalization of MPTS self-assembled Monolayers with Fluorescein-5-maleimide

In order to visualize the thiol patterned stamped on glass substrates by microcontact printing, the thiol patterns were further bound to the fluorescence probe namely fluorescein diacetate 5-maleimide. The glass substrates with grafted thiol patterns were immersed in solution consists of a micro molar of the fluorescence probe in basic phosphate buffer (pH 10)/DMSO (1:1) and left overnight. Then, they were removed, washed with water, acetone and dried over a nitrogen stream.

Characterizations

Characterizations were conducted on AFM of an Ntegra P8 from NT-MDT with NSG01 cantilever (resonance frequency 150 KHz, force constant 5.5N/m) mounted with Diamond Like Carbon (DLC) tips also purchased from NT-MDT) in tapping mode by using 1nm tip (resonant frequency 115-190Hz) from NT-MDT Co, Moscow, Russia. Surface analysis realized on XPS from The Thermo Scientific™ K-Alpha™. Confocal Fluorescence Microscopy (CFM) experiments were performed on Zeiss LSM 700 microscope.

RESULTS AND DISCUSSIONS



Scheme-1. A schematic diagram for patterning monolayer onto glass substrates by microcontact printing technique.

General approach

Overview of the experimental process as illustrated in Scheme 1. Alkyl-thiol SAMs were prepared by microcontact printing technique. Firstly, PDMS stamps were inked with MPTMS (20% v/v) and followed by stamping on glass substrate (i). Secondly, the alkyl-thiol monolayer bound to the substrate was characterized by AFM (ii). Finally, the substrate with alkyl-thiol monolayer was immersed in a solution of fluorescein diacetate 5-maleimide in a 1:1 phosphate buffer/DMSO mixture. It was characterized by CFM to confirm the presence of alkyl-thiol monolayer on the substrate.

Atomic force microscopy

Tapping mode AFM images revealed the morphology of SAMs of thiol grafted on the substrate surface. As can be seen from the topography image of Figure-2, the 2D image represented a monolayer of alkyl-thiol consist of 10µm bands spaced by 55µm (black and blue arrows respectively) with an image size of 100µm x 100µm. The height cross-sectional profile of the monolayer is 0.8±0.2nm as depicted in Figure-3 which illustrating the thickness of the thiol monolayer and matching the size of the MPTMS molecules (0.7±0.05nm) [7].

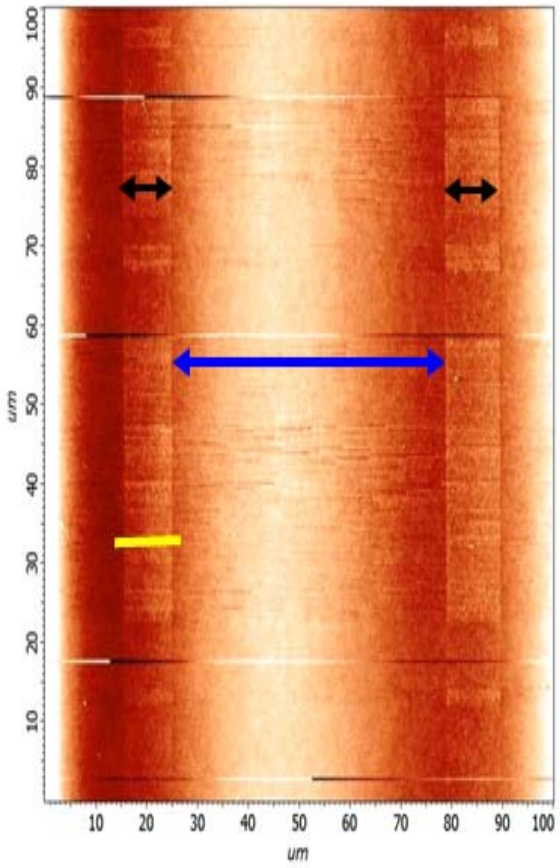


Figure-2. Characterization of AFM for thiol grafted on glass substrate; (a) AFM 2D topography image of alkyl-thiol monolayer with an image size of 100µm x 100µm. The black and blue arrows represent the 10µm band and 55µm space respectively.

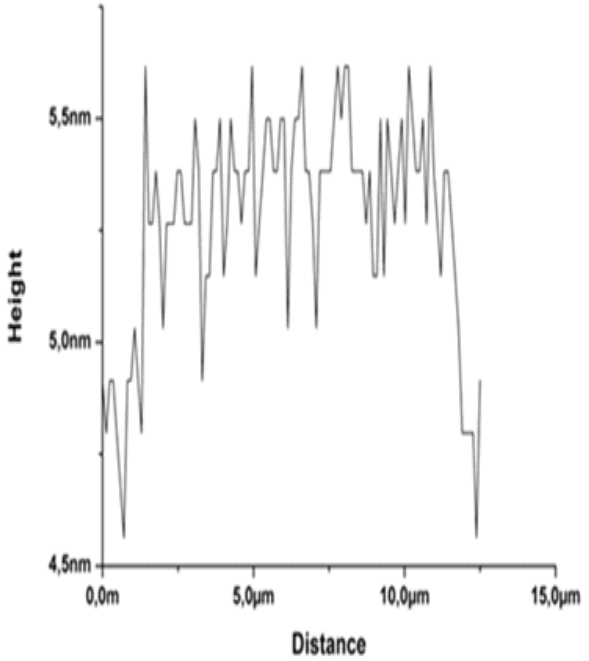


Figure-3. Corresponding height cross-sectional profile of the yellow line highlighted in Figure-2.

X-Ray photoeclectron spectroscopy (XPS)

XPS data in Figure-4 indicated there were two peaks in binding energy of 162.8 and 163.8eV respectively corresponding to the doublet structure in the S_{2p} region ($S_{2p3/2}$ and $S_{2p1/2}$ levels of the S energy levels). The ratio of peak area which is 2:1 confirmed the thiol groups existed on the surface and they were covalently attached to the glass substrate (Scheme 1(ii)) [12].

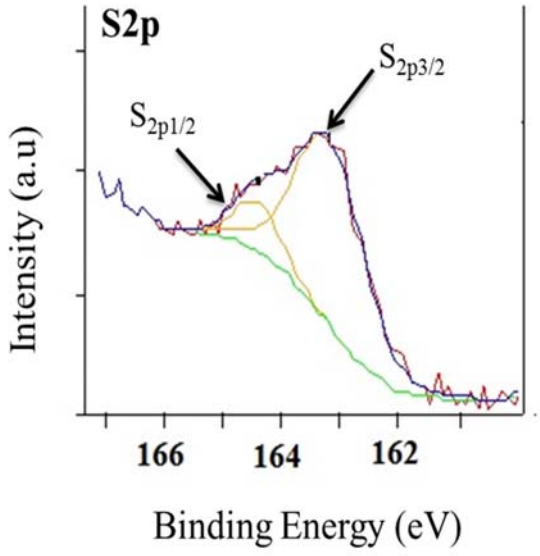
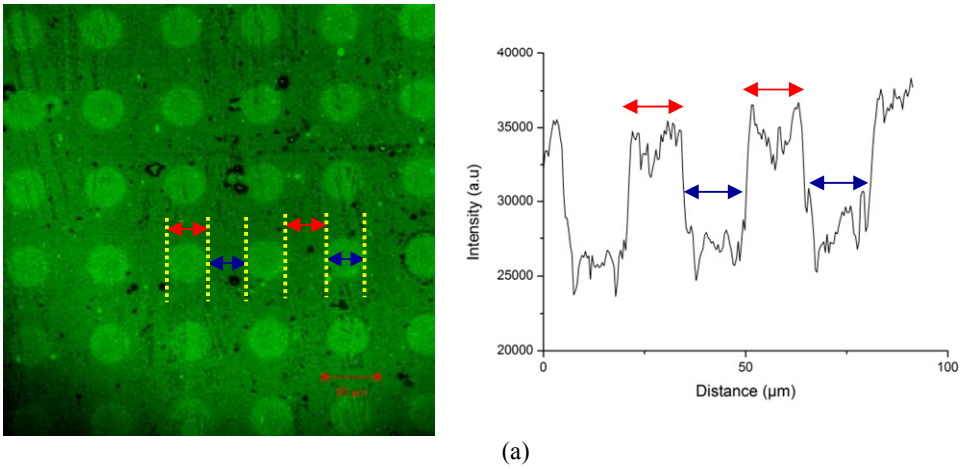
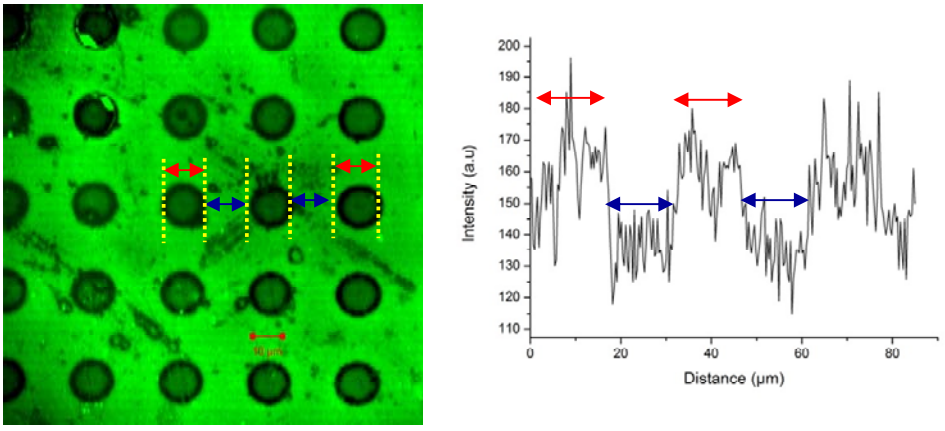


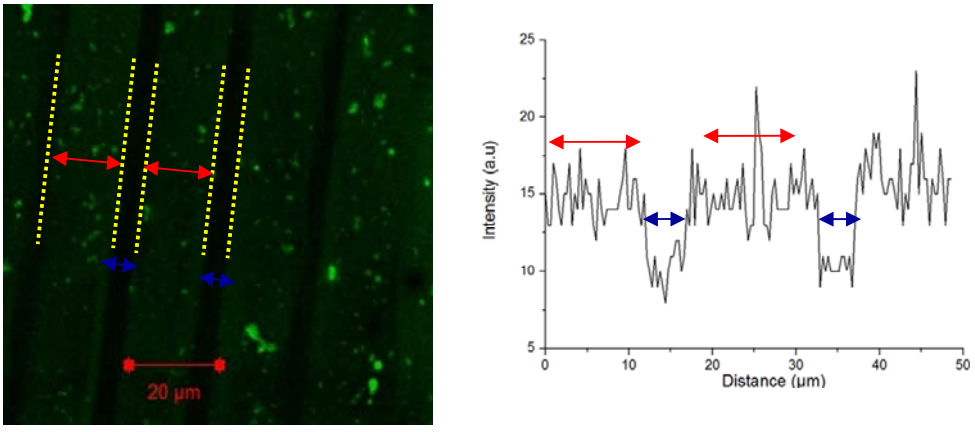
Figure-4. S_{2p} line in the XPS spectrum of MPTMS monolayer.



(a)



(b)



(c)

Figure-5. CFM images of thiol pattern labelled with a fluorescent probe. Dimension of (a) 10µm dots spaced by 10µm, (b) 1µm holes spaced by 15µm and (c) 10µm bands spaced by 15µm respectively. On the left pictures, the red and blue arrows indicate the patterned and un patterned areas. On the right pictures, the red and blue arrows illustrate the distinct intensity of patterned and un patterned areas respectively.

Confocal fluorescence microscopy (CFM)

The successful immobilization of thiol on the surface was investigated further by CFM. In general, the patterned areas consist of thiol monolayers with attached fluorescent probe should show higher intensity compared to unpatterned areas. In Figure-5, the images on the left indicate the images of pattern area (marked by red arrows) and the unpatterned area (marked by blue arrows). While the images on the right of Figure-5 represent the intensity profile of the pattern area (marked by red arrows) and the unpatterned area (marked by blue arrows). As revealed in Figure-5 (a), (b) and (c), the three different patterns namely 10µm dots spaced by 10µm, 10µm holes spaced by 15µm and 10µm bands spaced by 15µm showed the distinct intensity between the patterned (blue arrows) and unpatterned areas (blue arrows) where the patterned areas have higher intensity compared to unpatterned areas. Those results indicated that the alkyl-thiol monolayer has been successfully transferred to the glass substrate surface. It reacted with fluorescein diacetate 5-maleimide to be able to visualize under confocal fluorescence microscopy (Scheme 1(iii)).

CONCLUSIONS

In conclusion, by implementing a simple microcontact printing technique, SAMs of thiol could be covalently grafted on glass substrate. In particular, we believe this facile method could provide the possibility to further functionalize the SAMs for polymerization process or making the catalytic surface for subsequent chemical reaction which leading to various functional properties.

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