Microcontact Printing of an Alkylsilane Monolayer on the Surface of Glass

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This paper describes the use of microcontact printing (μCP) for patterning of self-assembled mono-layers (SAMs) of (3-aminopropyl)-triethoxysilane (APTES) and octadecyltrichloro silane (OTS) on the surface of glass and functionalization of alkylsilane monolayers. After activation of the glass surface, which was patterned with OTS using a poly(dimethylsiloxane) (PDMS) stamp, the remaining bars of the surfaces were treated with APTES and then treated with a dye solution. The characterization of printed silane compounds was confirmed using fluorescence microscopy on the basis of the reaction between terminal amine groups of APTES and thionylchloride of Rhodamine-B dye. Quantitative 3-dimensional profiling was performed for the whole modification process by converting of microscopic images to numerical dimensions.

Key Words: Microcontact printing, self-assembled monolayer, alkylsilane, modification.

Introduction

Several procedures exist for producing patterned mixed monolayers. Lithography lies at the heart of all of these techniques.[1] One popular method is microcontact printing (μCP), which is a soft lithographic technique that has been widely adopted to form chemical patterns or self-assembled monolayers (SAMs) on a variety of substrates in the past few years[2−9]. The technique provides a simple and rapid yet exceedingly powerful method of patterning molecules on surfaces. μCP uses an elastomeric stamp to print a variety of molecules in submicrometer resolution patterns without the need for dust-free environments or harsh chemical treatments.[10−12] The elastomeric stamp is generally made by curing poly(dimethylsiloxane) (PDMS) against a microfabricated silicon master, acting as a mold, to allow the surface topology of the stamp to form a negative replica of the master.[10] The masters are manufactured from photolithography, e-beam writing, micromachining, or relief structures etched into metals. The stamp is inked with the desired (silane) molecules, and those residing in the raised regions of the stamp are brought into contact with the host

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substrate when the stamp is printed. Therefore, the molecules transfer from the stamp to the substrate (glass) if they can interact more strongly with the substrate than with the stamp. For instance, in the patterning of silanes on the surface of glass, alkylsilanes form tight covalent bonds with Si-OH groups.[13]

In this study we investigated 2 different sets of alkylsilane monolayers on glass surfaces by PDMS stamp with parallel lines. In the first set, hydrophobic alkylsilane (OTS) was printed by μCP on the glass surface, and the remaining bare area was treated with a hydrophilic alkylsilane monolayer (APTES) according the procedure previously published.[14] After chemisorptions of APTES, the terminal amino group was reacted with Rhodamine-B. In the second set the position of alkylsilane printing was reversed. The mechanism of attachment between APTES monolayers and Rhodamine-B was investigated as a model for interfacial amine–Rhodamine-B reactions. The functionalized surfaces were characterized with quantitative 3-dimensional profiles by converting of microscopic images to numerical dimensions, which serves a main investigative tool for anchoring of SAMs on glass microscope slides. This principle utilizes differences in the functional properties of deposited materials to various surface sites.

Materials and Methods

Materials

All chemicals used for the preparation of SAMs and their μCP by surface reactions were of analytical grade, obtained from Merck, APTES from Sigma, OTS from Aldrich, poly(dimethylsiloxane) (PDMS) elastomer kit (SYLGARD 184), and curing agent (Dow Corning). Toluene was freshly distilled from sodium and dichloromethane from K_2CO_3. Glass microscope slides 2-mm thick were purchased from Isotherm, Germany. Prior to the μCP or monolayer preparation, the glass microscope slides were treated in boiling piranha solution (solution of 3:1 concentrated H_2SO_4 and 30% H_2O_2) for 1 h. Then the glass microscope slides were removed from the cleaning solution, rinsed with high purity water (18.2MQ cm, obtained from Ultrapure Milli-Q Reagent Water System Millipore), and dried in a stream of nitrogen until they appeared dry just prior to use for μCP or SAM deposition.

Microcontact printing (μCP)

A stamp for μCP was made by pouring a 10:1 mixture of PDMS (Dow-Corning SYLGARD silicon elastomer 184) and its curing agent over a photolithographically prepared master (previously produced at Hull University, Department of Chemistry) at 30 μm deep channels at 300 μm parallel lines. After the mixture was allowed to stand at room temperature for 1 h, further curing was performed in an oven at 60 °C for 1 h. Finally, the PDMS stamp was peeled away from the master. The stamp surface has a series of stripe-like convexities as shown in Figure 1. It can be seen that the PDMS stamp can be effectively used for patterning of surfaces and obtained more than one kind of molecule with the same parallel lines. After cleaning of microscopic slides, a 10 μL drop of the 2 mM APTES or OTS (0.4 w %) solution in toluene was dropped on the flat surface, either a microscopic slide or a petri dish. The PDMS stamp was placed on the dropped solution to spread the solution thoroughly over the surface of the stamp for about 15 s, and then it was dried under a stream of nitrogen. The stamp was brought into contact with a glass substrate and withdrawn after a contact period of about 15 s, and excess solvent was evaporated from the stamp under a stream of N_2. The stamped glass substrate was washed twice with toluene, dichloromethane, and ethanol to remove any

physisorbed material and it was dried under a stream of N_2. After μCP the slides were treated to silanize the remaining parts of the slide with OTS or APTES solutions by following the literature procedure.[14] Microcontact printed glass surfaces were obtained by stamping stripes of OTS or APTES and applying a second alkylsilane (hydrophilic or hydrophobic) onto the remaining bare hydroxylated surface regions.

(a)   (b)

Figure 1. Optical microscopic images of the PDMS stamps. The bar represents 300 μm. (a) cross-sectional view, (b) front view.

The experimental procedure is outlined in schematic form in Figure 2. As noted earlier, this attachment protocol results in partial monolayers of APTES with coverage of about 1 residue/nm^2,[14,15] as compared to coverages of about 2 residues/nm^2 reported in most literature studies of APTES monolayers prepared under anhydrous conditions.[16−19]

APTES-OTS patterned and derivatized glass microscope slides were placed in a solution of 0.1 mL of triethylamine and 15 mg of Rhodamine-B in 20 mL of acetonitrile. The reaction was allowed to proceed for 24 h at room temperature, followed by washing twice with acetonitrile, ethanol, and dichloromethane, and then followed by overnight drying in nitrogen atmosphere. The protocol for these stages is briefly presented in Figure 3.

An Olympus fluorescence (BX51/BX2-FLB3-000) microscope was used to obtain digital microscopic images of the printed molecules on the microscopic glass surfaces step by step during all the stages. The fluorescence source was provided by 100 W tungsten lamp using a 550 nm peak (BP520-550 excitation filter) a 570 nm peak (DM570 emission filter) plus a 590 nm dichroic beam (BA590) splitter. Microscope images of patterned surfaces were collected using a CCD camera (DP70 microcope digital camera, 12.5 million pixel resolution) giving a digital output of a maximum 356×300 pixels with 16-bit resolution of the light intensity in each pixel. The digital camera was connected to a PC and checked by digital image analysis, and then the images were saved. Scion Image (V.402) was used to convert the images from TIFF files to numerical image data, which were transferred to Microsoft EXCEL for subsequent conversion into absorbance values with short pixel by pixel height values.[14]
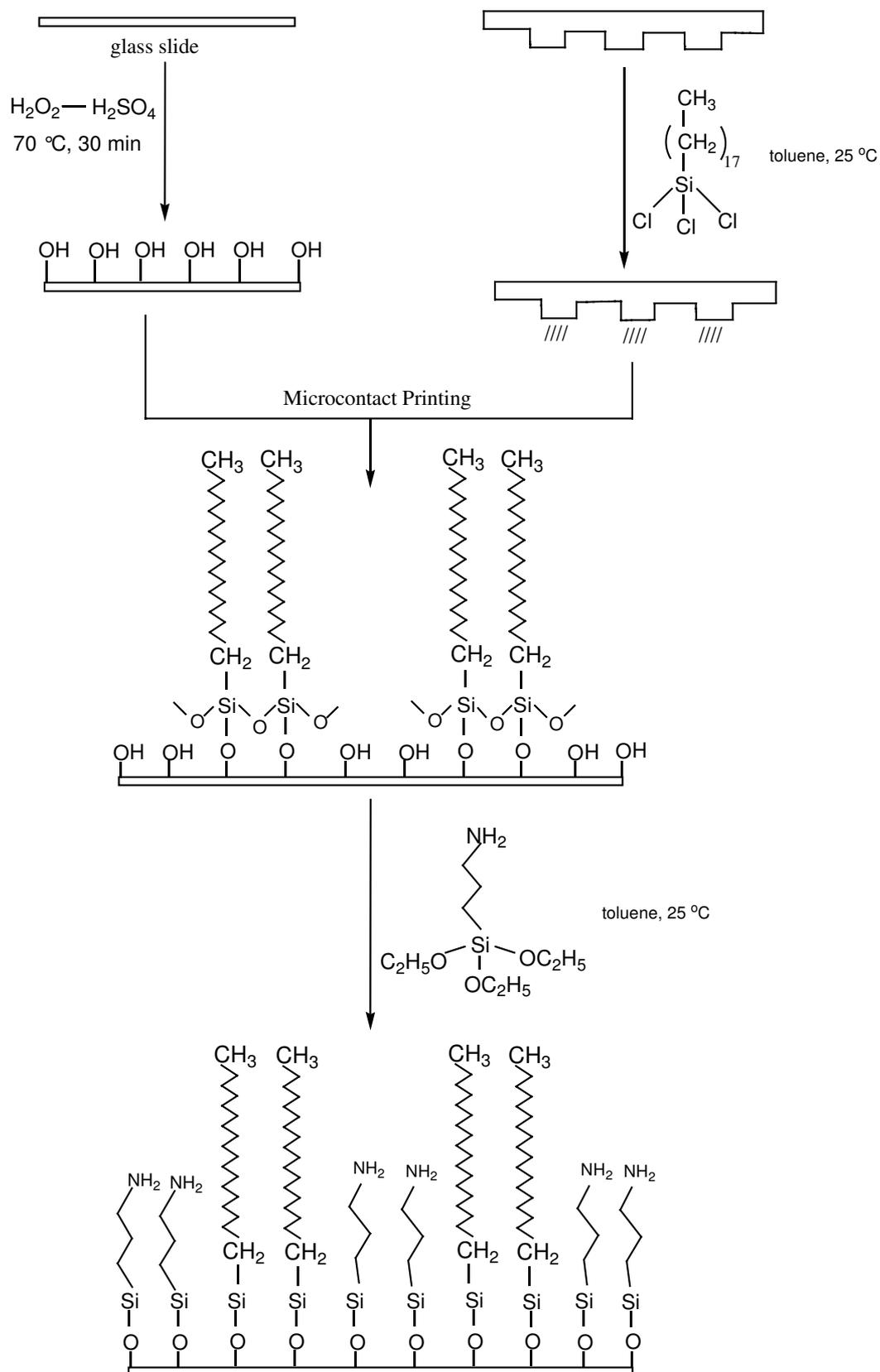
Figure 2. Schematic outline of the procedure for patterning of alkylsiloxanes on the glass surface.
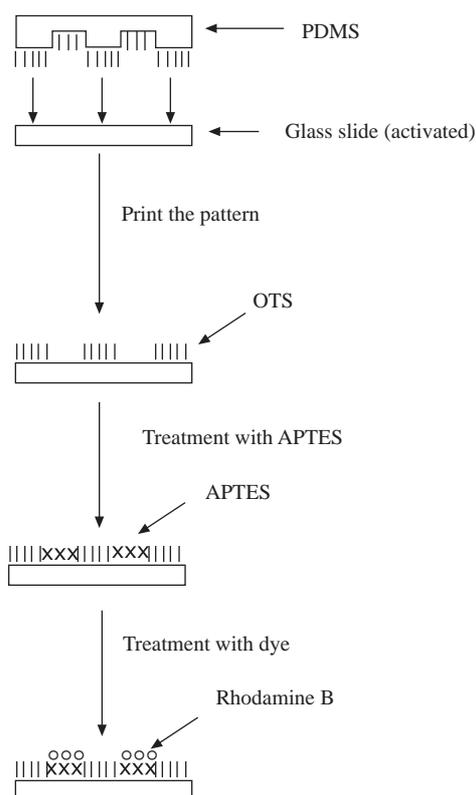
Figure 3. Surface modification of glass microscope slides with SAMs.

Results and Discussion

The initial experiments aimed to produce uniform SAMs of APTES or OTS (2 mM in anhydrous toluene) on glass microscope slides by μCP. Then unprinted surfaces of microscopic slides were treated with APTES or OTS with respect to the procedure in the literature.[14] After that the APTES monolayer was further functionalized, exploiting the reactivity of primary amine in the subsequent reaction with sulfonyl chloride in Rhodamine-B dye as presented in Figure 3. The structure and properties of the silane layer on the surfaces depend on the functionality of the compound attached to the functional group of silane, but also on the method used to apply the silane to the surface. Different methods for preparing SAM have been used. Among them, μCP is a new, fast, and very reliable method to produce SAMs.[2-4] The ideal case would be to form a monolayer of coupling agent to the surface where all silanol groups have reacted either with surface hydroxyl groups or silanol groups on neighboring silanes.

The surface functionalization process by using of both μCP and treatment in solution medium were controlled by taking of fluorescence images. As shown in Figure 4, OTS treated places showed almost no fluorescence, in contrast to the strong fluorescence observed on the surface of the APTES-coupled slide when the glass microscope slides were treated with Rhodamine B. The glass microscope slide cleaned with piranha solution was also treated with Rhodamine B solution. When the resulting patterned multilayers were immersed into a Rhodamine B dye solution for 4 h, the APTES layer adsorbs selectivity based on the reaction between amine groups of APTES with chloride groups in the Rhodamine B dye. It was found that the image was the same as the original one. These results suggested that amino groups were successfully

introduced onto the surface of the glass microscope slide.

The approach here is the introduction of 2 or more different elements that have different functionality within the matrix. Here we present an approach to assemble a hydrophilic/hydrophobic component array directed to corresponding regions of the surface. A further aim is to demonstrate the patterning of multilayers having different functionalities with high selectivity onto microcontact printed surfaces. Layer-by-layer self-assembled monolayers can provide functionality[20−23] as well as opportunities to increase adhesion properties between the multilayer surfaces and it has been pointed out that multilayer surfaces are tuned during the layer-by-layer assembly process to vary surface charge density, density of functional groups at the surface, film thickness, and wetting properties.[24−27]
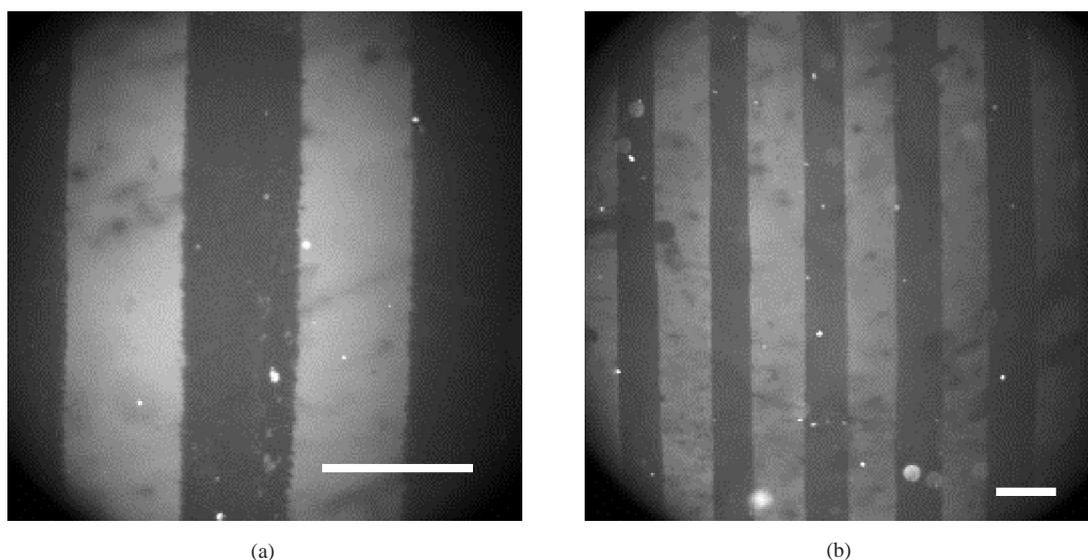

(a)   (b)

Figure 4. Fluorescence images of Rhodamine B-labeled alkylsilanes patterned by μCP onto a glass slide, a) μCP of OTS (0.4 w%) and treating with APTES reacted with dye, lens $\times$10, FITC filter, Exposure times 20 ms, bar 300 μm. b) the same image, lens $\times$4.0, FITC filter, Exposure times 93 ms, bar 300 μm.

Three-dimensional profiling of micron-sized channel networks for transparent "lab-on-a-chip" micro reactors from microscopic images was firstly quantified by Broadwell et al.[28] The process is based on spectroscopic imaging techniques such as UV-vis, IR, and Raman. In the process, the microscope image is converted to numerical dimensions with a maximum transmission wavelength matching the wavelength of the absorbance maximum of the dye solution. Digitized images of glass microscope slides silanized with APTES or OTS and then functionalized with Rhodamine B dye solution are determined pixel by pixel to yield a spatially resulted array of absorbance values. The array is then converted to optical path length values using the Beer-Lambert law, thereby providing 2-D and 3-D profiles of the network. From this fact, we applied this process for profiling of microscopic images of silane monolayers printed by μCP step by step during all stages of the modification process.[19] The process was described in detail previously.[14]

The 3-D profiles procedure is expressed as follows:[19]

$$A = \log\left\{\frac{I_{ref} - I_{dark}}{I_{sol} - I_{dark}}\right\}$$

where A is the absorbance represented by the Beer-Lambert law, and I_{ref} and I_{sol} are the transmitted

light intensities for reference and the dye solution, respectively. I_{dark} is the detector signal recorded in the absence of incident light, c is the concentration of absorbing spacers in the solution, d is the optical length, and ε is molar absorption coefficient.[19]

In Figure 5 the resulting 3-D profiles and in Figure 6 the resulting 2-D profiles of the patterned surfaces for all stages are illustrated. It is seen from these figures that the surface patterning process by μCP for SAM of APTES or OTS on glass microscope slides was successfully obtained. On the basis of these findings, the functionalization of amine-linked slides by treating with different heterobifunctional groups can be prepared for various applications.

In this work, we investigated SAMs of alkylsilane on glass and functionalization of silane monolayer with dye solution and their 3-D profiles were presented with Rhodamine-B dye. This study will be lead to further studies using SAMs containing molecules of different chain lengths carrying functional groups that will act as chemical tethers for macrocyclic compounds in different applications, such as chemical or biosensor, protein or enzyme immobilizations. We want to have a uniform distribution of long chain molecules in the mixed layer with different functionality either hydrophilic or hydrophobic properties and to give the most uniform properties of the surface.
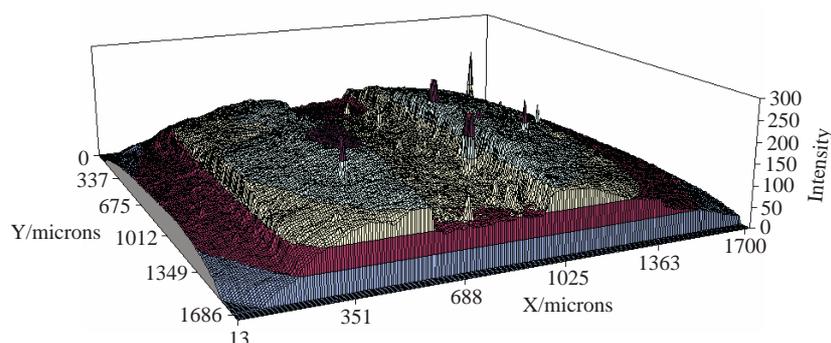

Figure 5a. 3-D profiles images of all the reaction stages for the modification process (the profiles represent the images in Figure 4a).
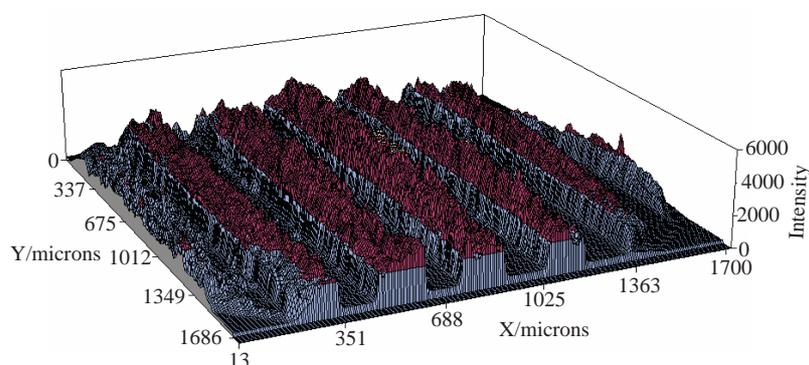

Figure 5b. 3-D profiles images of all the reaction stages for the modification process (the profiles represent the images in Figure 4b).
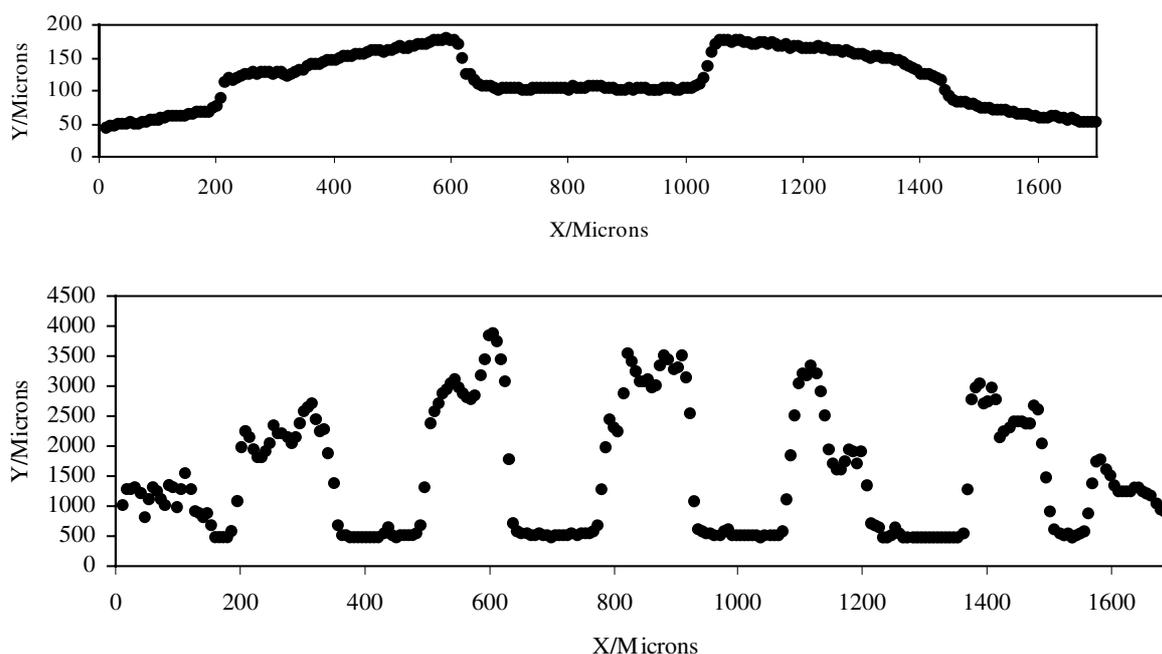
Figure 6. 2-D profiles images of all the reaction stages for the modification process (the profiles represent the images in Figure 4a and b).

Conclusion

SAM of APTES as well as other silane compounds on glass can be used for the immobilization of a variety of functional groups via surface reactions. It is well known that amine groups have reactivity towards many functional groups that can be incorporated to SAMs. Extensive characterization of amine groups of the APTES has been investigated and it was found that it is able to undergo surface reactions. Further research is underway to immobilize some biomolecules onto SAMs for various applications. Especially fluorescence microscopy has proven to be a valuable technique for the easy detection of interactions among the fluorophilic groups in the SAM. Particularly the quantitative dimensions of 3-D profiles have shown immobilization reactions sequentially.

It was demonstrated that the concept of selective deposition can be applied not only to patterning, but also to functionalization with different adhesion properties, fabrication of 2- or 3-D micro- and nanoscale structures for the creation of nano materials, polyelectrolyte multilayer films, templates for ordered layers etc. By manipulating the patterning as well as chemisorption conditions, it is possible to direct 2 different sets of functionalizing to different surface regions based on the interaction between the end functional groups. This method provides a flexible and versatile route to the fabrication of nanostructures and novel materials, and can be adopted utilizing different shaped patterned surfaces.

Acknowledgments

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