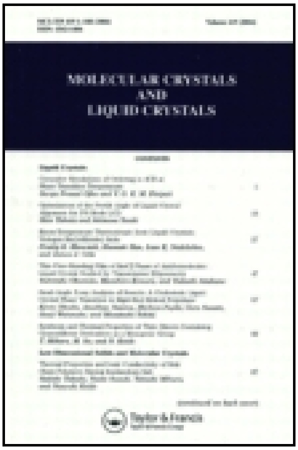

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Surface Modification with Functionalized Self-Assembly and Surface Characterization by Lateral Force Microscopy

Yun Kim [a] & Kwang-Salk Kim [a]
[a] Department of Chemistry, Pohang University of Science and Technology, San 31 Hyojadong, Namgu, Pohang, 790-784, Korea

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Surface Modification with Functionalized Self-Assembly and Surface Characterization by Lateral Force Microscopy

YUN KIM* and KWANG-SALK KIM
Department of Chemistry, Pohang University of Science and Technology, San 31 Hyojadong, Namgu, Pohang 790-784, Korea

Elastomeric poly(dimethylsiloxane) (PDMS) stamps were used for micro-contact printing (μ-CP) to pattern the adsorption of alkanethiolates on surfaces of gold on a scale of submicron. With this printing, organic surfaces patterned with well-defined regions exhibiting different chemical and physical properties have been produced. Au-coated mica substrates were treated with functionalized thiols to produce self-assembled monolayer (SAM) surfaces terminating with Br and OH groups by μ-CP method. Lateral force microscopy (LFM) has been utilized to characterize the adhesive interactions between substrates and probe tips that had been functionalized with SAMs which terminate with Br and COOH groups, respectively. LFM data exhibit that friction force between the probe tip and sample surfaces strongly depends on the functionality of both surfaces. This approach can be served as a method for mapping more complex and chemically heterogeneous surfaces.

Keywords: surface modification, functionalized alkanethiolate, self-assembly, lateral force microscopy, microcontact printing, friction

INTRODUCTION

Self-assembled monolayer (SAM) of alkanethiolates on the surfaces of gold has attracted attentions in surface sciences.[1]-[7] In particular, functionalized alkanethiol monolayers can provide a variety of surface properties through the variation of the surface functionality. Recently, SAMs have shown potential applications in many important systems requiring the chemical recognition such as biofunctional systems, chemical sensors and surface tribology of materials, etc.[8] In this study, microcontact printing (μ-CP) and solution deposition methods were utilized to modify the surface monolayers with functionalized alkanethiols $X\text{-}CH_2(CH_2)_{10}SH$ on a polycrystalline Au substrate on a scale of submicron. Alternating line-patterns of SAM surfaces with two functional groups, OH and Br, were examined in topography images obtained by atomic force microscopy (AFM) and friction images obtained by lateral force microscopy (LFM). LFM was also used to investigate adhesive interaction between patterned surfaces and modified probe tips with SAMs that terminate in Br and COOH groups, respectively. Lateral force images can be interpreted in terms of the frictional interaction between different functional groups to give rise to the basis for the chemical recognition of specific groups on the surfaces.

EXPERIMENTAL

Mercaptoundecane derivatives $X\text{-}CH_2(CH_2)_{10}SH$ were synthesized as described in elsewhere.[9]-[11] Topography and friction measurements were made with Digital Instruments Nanoscope III multimode microscope that can be operated in atomic force and lateral force microscopy modes at the same time in air. Poly(dimethylsiloxane)(PDMS, Sylgard 184) from Dow Corning has been used to prepare elastomeric stamps according to the published procedure. [12]-[14] Functionalized self-assembly was prepared on the surface of gold by μ-CP and solution deposition methods.[15]-[16] μ-CP method is described in Figure 1. LFM probe tips were coated with polycrystalline gold by thermal evaporation followed by chemical modification with functionalized alkanethiolates by solution deposition method (Figure 1 (b)).

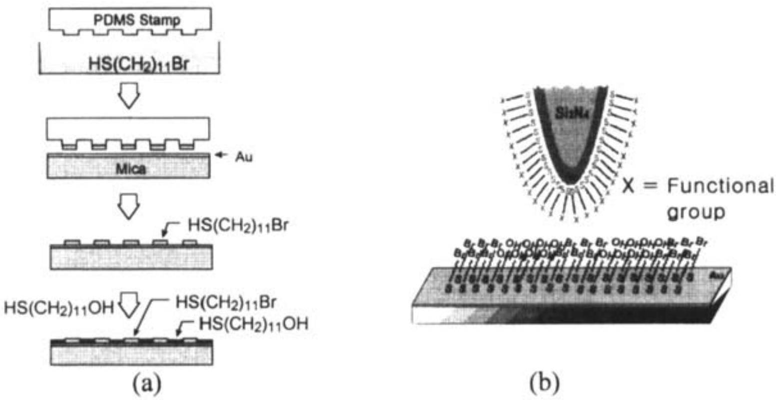

FIGURE 1 (a) Schematic diagram of microcontact printing method.
(b) Chemically modified probe tip and sample surface.

RESULTS AND DISCUSSION

Atomic force microscopy (AFM) was utilized to measure the topography of self-assembly surfaces obtained from microcontact printing methods. AFM images of SAMs composed of undecanethiols containing Br and OH groups, respectively, clearly exhibit the alternating line patterns which show the topographic differences. The topographic change in the images is due to the difference of radii of the two groups. Radius of Br group is 1.142Å while the oxygen radius of OH group is 0.66Å. Resulting difference in diameter of the two is about 0.96 Å. Average height difference from the measured AFM data is 0.9 ± 0.1 Å (AFM images of Figures 2 and 3). It is, therefore, certain that protruding lines are corresponding to the Br groups and the background is composed of the OH groups.

Modified AFM tip with functionalized alkanethiols were applied to lateral force microscopy. LFM images scanned by modified probe tips are compared with AFM data at the same time. LFM images scanned by normal tip show that frictional image is very similar to the topographic data. Frictional interactions between sample surfaces and modified probe tips were examined simultaneously using the combined force microscopy. Scanning by Br-modified probe tip provides almost same results as normal probe does. With Br-probe, noticeable frictional change was not observed in LFM image comparing to the AFM data (Figure 2). However, COOH attached probe tip shows the frictional inversion in the LFM images, even though AFM image by the very tip is quite similar to the AFM images by other tips (Figure 3). With COOH probe, Br-line patterns on the SAM surfaces are not protruding any more in LFM image and the area is even darker in image contrast which indicates lower friction area. This indicates that OH functional group is exhibiting strong H-bond interaction with COOH group which leads to high friction in LFM images. This strong interaction between OH and COOH groups even can compensate the topographical contrast in AFM images. However, Br-OH interaction is relatively weaker than Br-Br and OH-COOH. Similar results have been reported in COOH-COOH system.[17]

Conclusion

Submicrometer scale patterning with different functional groups on the self-assembled monolayer surfaces has been achieved by μ-CP method and the surfaces were characterized by combined force microscopy. It is certain that from the LFM data the frictional interaction between the tip with a certain functional group and sample surfaces modified with OH and COOH groups exhibit strong adhesion force leading to the chemical recognition. LFM with chemically modified probe tips can play important roles in investigating functional group and molecular recognition of many systems on the substrate surfaces.

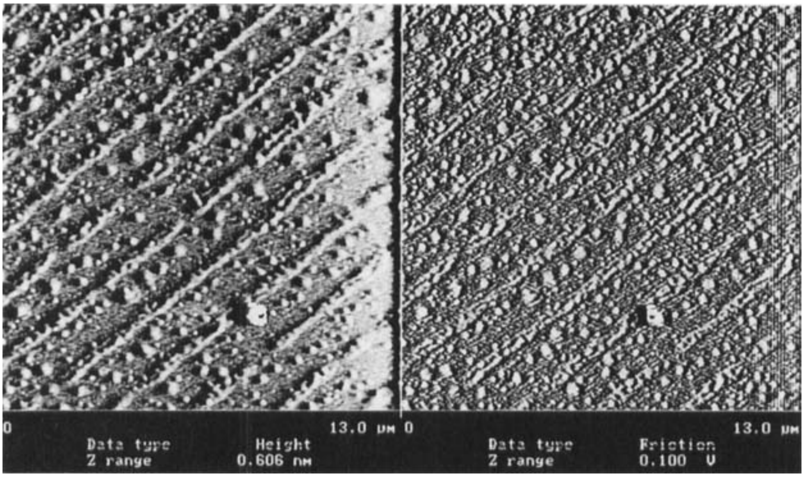

FIGURE 2 AFM (topography, left) versus LFM (friction, right) images of patterned surface with terminating with OH and Br groups scanned by a Br probe tip.

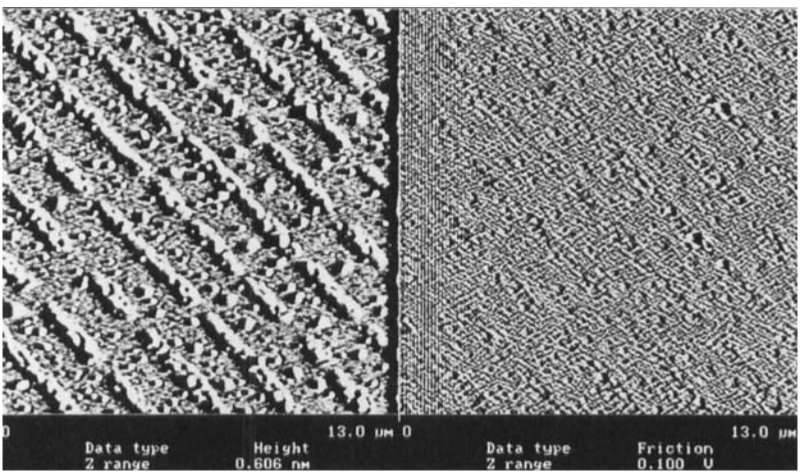

FIGURE 3 Topography (left) versus friction (right) images of patterned surface with terminating with OH and Br groups scanned by a COOH probe tip.

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