# Site-selective Coating of Polymer Thin Film Prepared by the Ink-jet Method on the Patterned Fluoroalkylsilane Monolayer Substrate

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(Received March 18, 2005; CL-050371)

The purpose of this study is to establish the fundamental technology of site-selective coating of polymer thin film utilizing wetting contrast of patterned fluoroalkylsilane monolayer/silanol (Si–OH) surfaces. Polystyrene (PS)/xylene solution was coated on the patterned surface with wetting contrast by ink-jet method. The patterned PS ultrathin films were selectively formed on lyophilic Si–OH areas.

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In recent years, site-selective deposition of functional materials on well-defined micropatterned surfaces has been actively studied for practical applications such as electronic, optical, and medical devices.[1] Several investigations[2,3] in these research fields have focused on coating technologies applied to the patterned surface with components of different wettability, with the intention for producing low-cost devices. On the other hand, ink-jet technology, which is known as the most representative coating method, can coat only specific areas with small quantities of micro droplets. However, it is difficult to form a thin film with an accuracy of the position less than 10 μm in a X–Y plane, as the required droplet size in the ink-jet method is over several ten μm and this method has an positioning accuracy of over several tens μm.[4] Wang et al. reported that the polymer thin film prepared by ink-jet method dewetted on a line patterned lyophobic mesa structure with submicrometer width and 30–80 nm thickness.[5] However, the fabrication of mesa structure was very complicated.

In this paper, the authors report that submicro- and micrometer scale "site-selective coating" of PS/xylene solution on "flat" patterned substrates, which were fabricated through photodecomposition of the fluoroalkylsilane monolayer by vacuum ultra violet (VUV) irradiation.[6,7] We propose a novel microfabrication method with a combination of the fluoroalkylsilane monolayer-patterned substrates and ink-jet method. Finally, the fabrication of polymer ultrathin film with ca. 500 nm line width using the patterned substrate with a submicrometer line is reported.

Perfluorohexylethyltrimethoxysilane monolayer [$R_f$, $CF_3(CF_2)_5CH_2CH_2Si(OCH_3)_3$] and *n*-decyltriethoxysilane monolayer [$R_h$(C10), $CH_3(CH_2)_9Si(OC_2H_5)_3$] prepared by a chemical vapor adsorption method were used as a substrate.[8] The patterned organosilane monolayers were fabricated by photolithography with VUV light with $\lambda = 172$ nm. Homogeneous monolayers were photodecomposed under irradiation of VUV light through a photomask with a line and space. Finally, the monolayer under the VUV-irradiated portion was removed as volatile species, and Si–OH residues were formed. In the present study, the effects of asperity of the patterned surface on wetting can be ignored because the height difference between the $R_f$ and Si–OH areas is less than 1 nm.[6,9] Therefore, the wetting phenomena in the present study would only be governed by surface chemistry. All experiments were carried out under atmospheric pressure and at room temperature ($298 \pm 2$ K).

The wetting characteristics, i.e., static contact angle and surface free energy ($\gamma_s$), of three homogeneous surfaces, which are the components of the patterned surface, were evaluated.[8] The $\gamma_s$ were decreased in the order of Si–OH (76 mJ m$^{-2}$) > $R_h$(C10) (25 mJ m$^{-2}$) > $R_f$ (14 mJ m$^{-2}$). Therefore, $R_f$ is able to repel 3.0 wt % polystyrene (PS)/xylene solution used as an ink of ink-jet. Receding contact angles $\theta_r$ of PS/xylene solution measured using the sliding angle method were 55° for $R_f$, and 19° for $R_h$(C10), respectively, in a reflection of these $\gamma_s$. From this property, chemical patterned substrates with the $R_f$ component lead to the successful "site-selective coating" by the ink-jet method.

Figures 1a and 1b show optical micrographs of PS thin films coated by the ink-jet method on (a) $R_f$/Si–OH and (b) $R_h$(C10)/

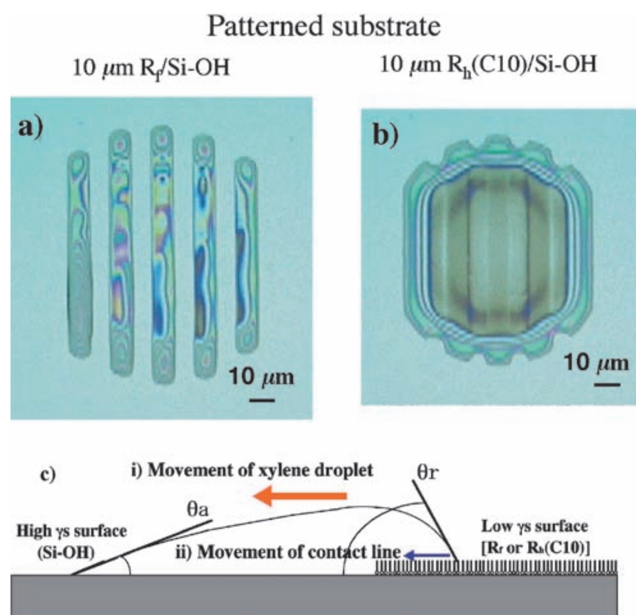


**Figure 1.** Optical micrographs of polymer thin films coated by ink-jet method. PS/xylene solution was applied on (a) $R_f$/Si–OH and (b) $R_h$(C10)/Si–OH patterned surfaces with 10 μm line width. (c) Schematic representation of a moving xylene drop and contact line at the line-patterned surface.

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Si–OH patterned surfaces with a 10 μm line width. In the case of (a) $R_f$/Si–OH, perfect line-patterned films were formed. In contrast, when the less lyophobic patterned surface was employed, i.e., the case of the (b) $R_h$(C10)/Si–OH substrate, PS thin film was not formed along the pattern.

The complete breakup of PS thin film on $R_f$/Si–OH substrates is caused by (i) the spontaneous drop motion along the direction perpendicular to the line and (ii) the pinning of the receding contact line. Figure 1c shows schematic representation of a moving xylene drop and contact line at the line-patterned surface. (i) The driving force for a spontaneous drop movement is the unbalanced Young force,[10] $F$, that results from the difference in wettability between the front and backsides of the droplet:

$$F = \gamma_l(\cos\theta_a - \cos\theta_r), \quad (1)$$

where $\gamma_l$ is the surface tension of the liquid, and $\theta_a$ and $\theta_r$ are the advancing contact angle of the high surface energy phase and the receding contact angle of the low surface energy phase for the droplet, respectively. This equation indicates that when the difference in wettability between lyophilic and lyophobic regions is large, i.e., the "contrast in wettability" is high, movement of the xylene drop on the patterned substrate takes place. In this case, $F$ is ca. 12 mN m$^{-1}$ for $R_f$/Si–OH [$\theta_r$ : 55° ($R_f$), $\theta_a$: ≅0° (Si–OH)], and ca. 2 mN m$^{-1}$ for $R_h$(C10)/Si–OH [$\theta_r$ : 19° ($R_h$(C10)) $\theta_a$: ≅0° (Si–OH)], respectively. (ii) The contact line is usually pinned when the static contact angle becomes much smaller than 90°.[11] Therefore, since $\theta_r$ is 19° for PS/xylene solution on $R_h$(C10), it is expected that the contact line on $R_h$(C10) area is pinned before the contact line reaches the $R_h$(C10)/Si–OH interfacial line. On the other hand, the contact line of the xylene droplet on the $R_f$ area ($\theta_r = 55°$) recedes without pinning to reach the interfacial line. The diameters of the 1 μL PS/xylene droplet on the homogeneous $R_f$ or $R_h$(C10) substrate during evaporation were measured to verify the above hypothesis. The droplet diameter for $R_f$ decreased from 1.5 to 0.9 mm, whereas that for $R_h$(C10) was constant at 2.3 mm. From the results obtained above, it can be concluded that the breakup of PS thin film on $R_f$/Si–OH occurred due to this large contrast in wettability.

The apparent morphology of the film is also important factor for the device application. We focused on the width and thickness of the PS film coated on a $R_f$/Si–OH substrate. Figure 2 shows AFM images and line profiles of PS thin films on a $R_f$/Si–OH patterned substrate prepared by the ink-jet method. When the Si–OH width of the substrate was above 2 μm, the width of the PS thin film was in good agreement with that of the Si–OH region. On the other hand, when the Si–OH width was less than 1 μm, the width of the PS thin film decreased less than that of the Si–OH width. Using a substrate with a 0.7 μm Si–OH width, a PS thin film with a 0.5 μm width and 25 nm thickness was formed (Figure 2a). For the film thickness, when the Si–OH width of the substrate was less than 2 μm, the homogeneous PS thin film was formed in the Si–OH region. In contrast, when the Si–OH width was above 5 μm, a higher height region at the edge along the line-patterned contact line (Figure 2c) was observed. This phenomenon corresponds to a "ring-like deposit"[12] occurring on the homogeneous substrate, and can be explained by evaporation and fluid flow. Furthermore, the line width (0.7–20 μm) of the PS thin film was nearly proportional to the film thickness with a constant aspect ratio (thickness/width: 0.02–0.05). This result indicated that the height of the polymer solution on the lyophilic region was proportional to the line width.

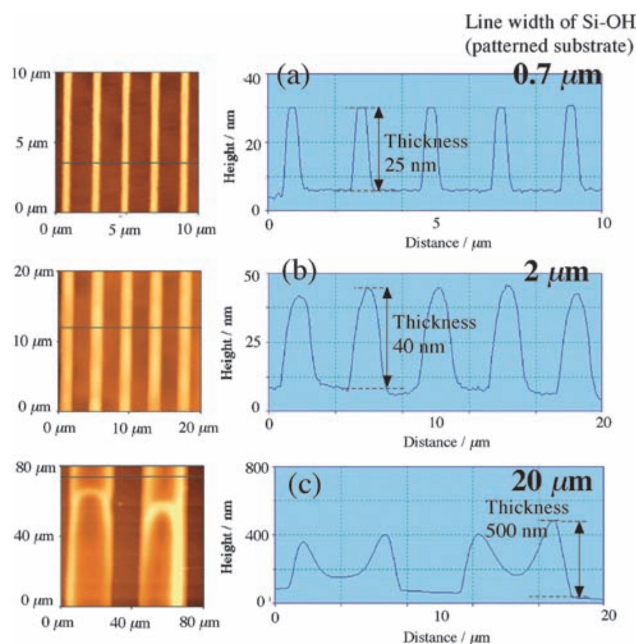


**Figure 2.** AFM images and line profiles of polystyrene thin films on $R_f$/Si–OH patterned substrate prepared by ink-jet method.

In summary, we have proposed herein a novel microfabrication method with a combination of the fluoroalkylsilane monolayer-patterned substrates and ink-jet method to produce low-cost devices. We have shown that, i) using a fluoroalkylsilane monolayer-patterned substrate leads to the formation of a complete line-patterned PS thin film with a line width of ca. 500 nm by the ink-jet method; ii) the width and thickness homogeneity of PS thin film can be controlled by the width of lyophilic region.

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Published on the web (Advance View) June 4, 2005; DOI 10.1246/cl.2005.916