

Site Specific Fabrication of Polystyrene Ultrathin Films onto the Patterned Organosilane Monolayer Surfaces by the Ink-Jet Method

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The line-patterned fluoroalkylsilane (R_f) monolayer/Si-OH was fabricated in order to control the wetting behavior of polymer solution since fluoroalkylsilane has extremely low surface energy (γ) and the Si-wafer shows extremely high γ . Environmental scanning electron microscopic (SEM) observation of water condensation revealed that the water was selectively condensed on the Si-OH region. Dynamic and static contact angle measurements revealed the macroscopic anisotropy of contact angles on parallel and perpendicular directions to the lines. Droplets of [poly(3,4-oxyethyleneoxythiophene)/poly(styrene sulfonate)] (PEDOT/PSS) water dispersion and xylene solution of polystyrene were deposited on the 10 μ m line-pattern using inkjet technique from the orifice with a diameter of 50 μ m. The (PEDOT/PSS) water dispersion was not selectively wet on the hydrophilic Si-OH line. On the other hand, it was revealed that the xylene solution was repelled from the oleophobic R_f surface and the PS film with ca. 500nm width was selectively formed on the bare Si-wafer surface.

Key words: Fluoroalkylsilane monolayer, Patterned monolayer, Wetting anisotropy, Ink-jet method, Polymer thin films

1. INTRODUCTION

Site-selective deposition of functional molecules 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 intent of fabrication of low-cost devices. In this coating process, because the polymer solution is site-selectively wetted reflecting the pattern shape, the wetting property must play an important role in the formation of patterned polymer thin film. However, the relationship between site-selective wetting and coating behavior has not yet been clarified. 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 less than 10 μ m in a X-Y plane, as the required droplet volume in the ink-jet method is over several ten μ m and this method has an alignment accuracy of over several tens μ m.[2] In this paper, micro scale "site-selective wetting" of pure liquids on patterned substrates, which were fabricated through photodecomposition of the fluoroalkylsilane monolayer by vacuum ultraviolet (VUV)-ray irradiation[4] is discussed. We then propose a novel microfabrication method with a combination of the fluoroalkylsilane monolayer patterned substrates and ink-jet method. This combination allows

"site-selective coating" of polymer solution, and the mechanism is discussed from the perspective of the wetting of pure liquids. Finally, the fabrication of polymer ultrathin film with ca. 500 nm line width using the patterned substrate with a submicrometer line is reported.

2. EXPERIMENTAL

Homogeneous monolayers of organosilanes were prepared by the chemical vapor adsorption (CVA) method. The cleaned Si-wafers were placed into a Teflon container with liquid organosilane under a nitrogen atmosphere at 373 K for 2-3 h. Perfluorohexylethyltrimethoxysilane [R_f , $CF_3(CF_2)_5CH_2CH_2Si(OCH_3)_3$] and n-decyltriethoxysilane [$R_h(C10)$, $CH_3(CH_2)_9Si(OC_2H_5)_3$] monolayers prepared by a CVA method were used as a substrate. The patterned organosilane monolayers were fabricated by photolithography with vacuum ultra violet (VUV) light with $\lambda=172$ nm. The CVA method makes it possible to prepare amorphous alkylsilane monolayers with few defects and high uniformity.[5] Therefore, the monolayer prepared by the CVA method has an advantage over that prepared by LB or a chemical solution adsorption method for patterning. Homogeneous monolayers were photodecomposed under irradiation of VUV light through a photomask with a line and space. Photoirradiation of the VUV light causes the dissociation of covalent bonds such as C-C, C-H, and Si-C bonds accompanying oxidation with

active oxygen species generated by photoexcitation of atmospheric oxygen molecules.[6] Finally, the monolayer under the VUV-irradiated area was removed as volatile species, and Si-OH residues were formed.

The line/space ratio of the photomasks was 1/1, except for the space width of 0.7 μm , for which the ratio was 1.3/0.7. The relationships between the space width of the photomask and the Si-OH width (in parentheses) of the R_f /Si-OH patterned substrate were 0.7 μm (0.87 μm), 1 μm (1.08 μm), 2 μm (2.21 μm), 5 μm (6.02 μm), 10 μm (11.49 μm), and 20 μm (22.30 μm).

Ink-jet coating was performed with a homemade apparatus with a 50- μm diameter orifice. We used a 1.3 wt% PEDOT/PSS dispersion in water (Sigma-Aldrich, Co. Ltd.) and a 3 wt% PS (MW=250k, Acros Organics, Co. Ltd.)/xylene solution for ink. The diameters of the polymer thin film on the R_f /Si-OH substrate were 30-120 μm . All experiments were carried out under atmospheric pressure and at room temperature (298 ± 2 K).

3. RESULTS AND DISCUSSION

The morphology of the patterned organosilane monolayer surfaces was observed with FE-SEM (Field-emission SEM).[7] The Si-OH line-width measured by FE-SEM observation was 10-20 % wider than the space width of the photomask. Although the space width of the photomask was not completely equal to the patterned Si-OH width, we have designated the space width of the photomask as the line width of the patterned substrate in this paper.

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.[8] Therefore, the wetting phenomena in the present study would only be governed by surface chemistry.

The wetting characteristics, i.e., static contact angle θ_s and surface free energy γ_s , of three homogeneous surfaces, which are the components of the patterned surface, were evaluated. On the assumption that the contact angle values of water and methylene iodide on Si-OH surface are 0 deg., the surface free energies were calculated based on the method of Owens and Wendt.[9] The surface free energies 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 apolar organic solvents, i.e., n-hexadecane [θ_f : 66 deg. (R_f), θ_f : 33 deg. (R_h (C10))] and xylene [θ_f : 72 deg. (R_f), θ_f : 25 deg. (R_h (C10))]. From this property, substrates patterned with the R_f component lead to the successful "site-selective wetting" for pure liquids and "site-selective coating" by the ink-jet method.

The substrate with a different surface energy component allows site-selective wetting for pure liquids. If one phase of a micropatterned surface has an affinity towards a certain liquid, the surface can be utilized as a template for local liquid condensation. Fig. 1(a), (b) show the ESEM images of the water droplet on the R_f /Si-OH patterned substrate with (a) 1 μm and (b) 10 μm line width during the initial condensation process.

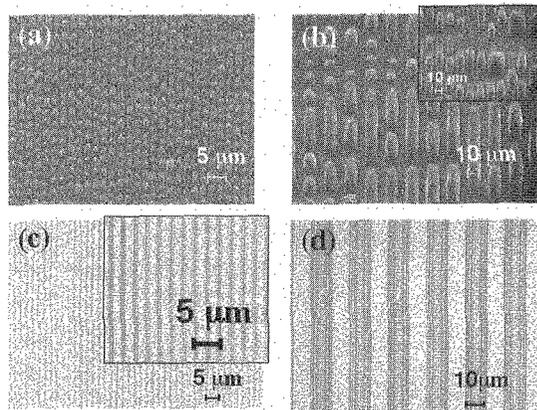


Fig. 1 (a),(b) ESEM images of water droplets formed by condensation and (c),(d) optical micrographs of line-patterned wetting of n-hexadecane on R_f /Si-OH patterned surfaces with (a),(c) 1 μm , (b),(d) 10 μm line width.

When the vapor pressure of the ESEM sample chamber was raised to 700 Pa [greater than the saturated vapor pressure of water (612 Pa) at 273 K], the water was selectively condensed on the Si-OH region as droplets because R_f was hydrophobic and Si-OH was hydrophilic, and water droplets were formed along the line direction. Further, the water droplet growth led to the growth of a liquid bulge across the adjacent R_f line because the water has large surface tension (72 mN m^{-1}). Finally, the water droplets coalesced with droplets on the adjacent line (see the inset image of Fig.1(b); therefore, complete growth in the line direction was not observed. The same results were obtained in the case of the other line width. Gau et al[10] have also reported a similar water bulge on a patterned substrate with ca. 40 μm hydrophilic line width. They concluded from "calculation of the free energies of the different droplet patterns" that this phenomenon occurred, when the contact angle of the growing water droplet was over 90 deg. The results with our substrates with line width less than 20 μm also originated from the same mechanism[10] discussed above.

On the other hand, Fig 1(c), (d) show optical micrographs of line-patterned wetting of n-hexadecane (27 mN m^{-1}) on the same R_f /Si-OH patterned surfaces. Thus, the low surface tension oil coated on the R_f /Si-OH substrate led to a cylinder-like thin film wetted along the liquidphilic area. These pure liquid results indicate that the liquids with lower surface tension are wettable along the patterned monolayer; i.e., control of site-selective wetting can be achieved by utilizing a patterned monolayer substrate.

Fig. 2(a)-(d) show optical micrographs of polymer thin films coated by the ink-jet method on (a)(c) R_f /Si-OH and (b)(d) R_h (C10)/Si-OH patterned surfaces with a 10 μm line width. PEDOT-PSS water dispersion and polystyrene (PS)/xylene solution were used as an ink for polymer coating. In the case of PEDOT-PSS water dispersion, incomplete site-selective thin film formation was observed. Although we investigated the film formation behavior in the case of half or one-third

dispersion concentrations, the same result was obtained. It is considered that the liquid bulge due to high liquid surface tension, similar to the pure liquid case (Fig. 1(b)) causes imperfect film formation. On the other hand, in the case of a PS/xylene solution on (c) R_f /Si-OH, perfect line-patterned films were formed. As described above, the coating behavior of polymer solution by the ink-jet method (Figs. 2(a), (c)) resembles the wetting of pure liquid (Figs. 1(b), (d)). Of course, we realize that the breakup of a polymer thin film by the ink-jet method is affected by the several factors, including the solution concentration, [3] the moving velocity of the substrate, [3] the evaporation rate of the solvent, [11] the substrate temperature, [12] etc. Further study is now in progress to clarify these factors.

When the less hydrophobic patterned surface was employed, i.e., the case of the (d) R_h (C10)/Si-OH substrate, PS thin film was not formed along the pattern. We can explain that the complete breakup of PS thin film on R_f /Si-OH substrates is caused by (i) the spontaneous drop motion due to the difference in surface free energy of R_f and Si-OH surfaces and (ii) the pinning of the receding contact line. Fig. 2(e) shows schematic representation of a moving xylene drop and contact line at the line-patterned surface. (i) The driving force for a spontaneous drop motion is the unbalanced Young force, [13] F , that results from the difference in wettability between the front and backsides of the

advancing liquid drop:

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

where γ_l is the surface tension of the liquid, and θ_a and θ_r are the advancing contact angle of the high surface free energy phase and the receding contact angle of the low surface energy phase for the droplet, respectively. This equation shows that when the difference in wettability between liquidphilic and liquidphobic regions is large, i.e., the "contrast in wettability" is large, the movement of the xylene drop on the patterned substrate takes place. In this case, F is ca. 15 mN m^{-1} for R_f /Si-OH [θ_f : 72 deg. (R_f), θ_a : ≈ 0 deg. (Si-OH)], and ca. 2 mN m^{-1} for R_h (C10)/Si-OH [θ_f : 25 deg. (R_h (C10)), θ_a : ≈ 0 deg. (Si-OH)], respectively. (ii) The contact line is usually pinned when the static contact angle becomes much smaller than 90 deg. [14] Therefore, since θ_f is 25 deg. for xylene 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 ($\theta_f = 72$ deg.) recedes without pinning to reach the interfacial line. The diameters of the $1 \mu\text{L}$ PS/xylene droplet on the homogeneous R_f or R_h (C10) substrate during evaporation were measured to verify the above hypothesis. In consequence, the droplet diameter for R_f decreased from 1.5 mm to 0.9 mm. In contrast, that for R_h (C10) was constant at 2.3 mm. From the results obtained above, it can be concluded that the acceleration of the breakup of PS thin film on R_f /Si-OH occurred due to this large contrast in wettability.

The 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 3 shows AFM images and line profiles of PS thin

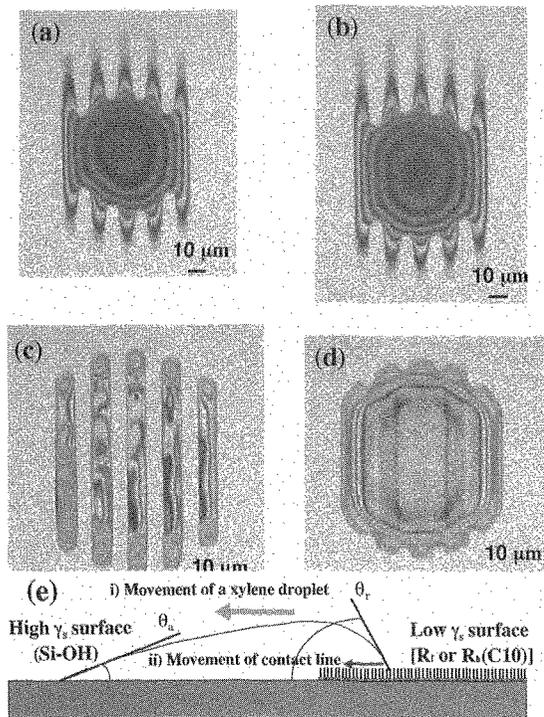


Fig.2 Optical micrographs of polymer thin films coated by ink-jet method. (a)(b) PEDOT-PSS water solution and (c)(d) polystyrene/xylene solution were coated on (a)(c) R_f /Si-OH and (b)(d) R_h (C10)/Si-OH patterned surfaces with $10 \mu\text{m}$ line width. (e) Schematic representation of a moving xylene drop and contact line at the line-patterned surface.

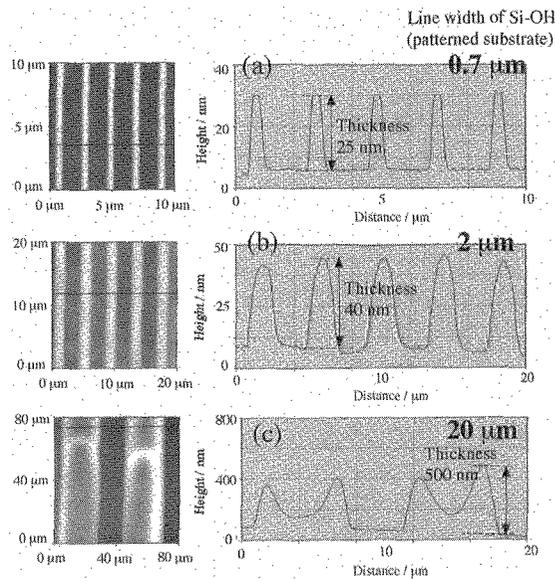


Fig.3 AFM images and the height profiles of polystyrene thin films on R_f /Si-OH patterned substrate prepared by ink-jet method.

films on a Rf/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 by half 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 was formed (Fig. 3(a)). 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 (Fig. 3(c)) was observed. This phenomenon corresponds to a "ring-like deposit"[12, 15] 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 liquidphilic region was proportional to the line width.

In summary, we have proposed a novel microfabrication method with a combination of the fluoroalkylsilane monolayer patterned substrates and ink-jet method to fabricate low-cost devices. It was revealed that, a) the breakup property of polymer thin film, which coated by the ink-jet method on alkylsilane monolayer substrates, parallels the wetting property of pure liquid; b) 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; c) the width and thickness homogeneity of PS thin film can be controlled by the width of liquidphilic region.

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