Effect of physical Properties on Micro-Structured Surfaces for Hydrophilic Control

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The wettability of solid surfaces can be caused artificially by chemical or structural effects. Property control by the former chemical effect has been applied to various products and has been put into practical use. However, it is not suitable for permanent use due to the possibility of chemical property changes over time. In other words, it is necessary to repeat the treatment again, and cost is one of the issues. For this reason, the attention is being paid to the structural effects of this wettability, which are manifested by micro-structured surfaces. However, the appropriate microstructure to achieve the desired wettability is not well understood. Therefore, many studies have been carried out worldwide to control wettability, i.e. hydrophobicity and hydrophilicity, by using microstructures. This study focused our investigations on the hydrophilicity among these properties. In this study, regular micro-structured surfaces with a regular arrangement of cylinders on a solid surface were fabricated using photolithography and reactive ion etching (RIE). The vertical tilt and height of the cylinders were adjusted by controlling the RIE processing conditions using single crystal silicon and glass as working materials. The effects of these changes on hydrophilicity and droplet shape were investigated. As a specific implementation method, patterning was carried out by photolithography using SU8 resist on single crystal silicon or glass substrates, and using this as a mask, a mixture of CF4, SF6 and O2 gas were used in the etching process. The similarities and differences in fabrication methods and properties such as hydrophilicity of micro-textures on single crystal silicon and glass substrates were investigated.

1. Introduction

Currently, numerous products utilize the wettability of solid surfaces. The wettability encompasses a wide range, from water-repellent hydrophobicity to water-attracting hydrophilicity. The former hydrophobicity has a wide range of applications in various fields, such as coatings on car surfaces [1]and the underside of yogurt lids [2]. On the other hand, the later hydrophilicity offers advantages, such as the ability to spread liquid droplets across a solid surface, facilitating the removal of adherent dirt or debris by allowing them to be washed away [3]. Due to these benefits, the control of wettability is an essential technology in a wide array of fields, including the building exterior, printing equipment [4], rainwear and swimwear [5], and optical instrument lenses [6]. Generally, the wettability is assessed by the contact angle formed when a liquid comes into contact with a solid surface [7]. This study has adopted a similar evaluation based on contact angle .

The wettability of solid surfaces has been the subject of extensive researches. A significant portion of these researches have focused on hydrophobicity [8], [9], [10]. However, as above mentioned, the hydrophilicity, with its potential to reduce surface resistance and remove contaminants through water-assisted removal, holds promise for application across various fields.

The hydrophilicity can be categorized into chemical and physical one. The chemical hydrophilicity is achieved through the use of chemical coatings, which are easy to apply but have limited durability, leading to wear and tear with repeated use. Consequently, the chemical hydrophilicity tends to be short-lived compared to physical one, necessitating regular maintenance. In contrast, the physical one is obtained by imparting microstructures onto the solid surface, offering a semi-permanent hydrophilic effect as long as these microstructures remain intact. However, the introduction of such microstructures, often realized through nano and micro scale manufacturing [11], tends to be more costly than chemical approaches. Therefore, this study aims to achieve physical hydrophilicity more easily by utilizing microstructures fabricated on a microscale.

Furthermore, previous researches especially ours, on microstructures has predominantly focused on in case of silicon substrates [12]. It is evident that if the findings from research on silicon substrates can be applied to other materials, the field of microfabrication could advance significantly. Therefore, this study also investigated the similarities and differences in microstructures formed on glass substrates, which have a similar structure to silicon. By conducting research on both silicon and glass substrates, this study seeks to lay the groundwork for realizing microfabrication for the hydrophilicity across a wider variety of materials.

2. Experimental methods

2.1 Fabrications of Micro-structured surface

This study used photolithography and Reactive Ion Etching (RIE) for fabrication of microstructure. The resist is used for microstructure on the Silicon and grass substrate. And the resist patterns were transferred by RIE to the substrate.

Mask patterns are circular holes with micrometer order. Each pattern has a different circle diameter, pitch, and structural angle. All patterns were transferred into resist on a silicon substrate at the same time.

【Equipment】

- Hot Plate: ND-1, AZONE
- Spin Coater: MS-B100, MIKASA
- Exposure Device: M-IS, MIKASA
- Reactive Ion Etching Device: BP-10NRTK, SAMCO
- Optical Microscope: ST30RDL, AZONE
- Optical Microscope: ECLIPSE LV150, NIKON
- Scanning Electron Microscope (SEM): ERA-600, ELIONIX
- Contact Angle Measurement device: DMs-401, Kyowa Interface Science

【Chemicals】

- OAP: Tokyo Ohka
- SU8-3025: Nihon Kayaku

【Exposure conditions of resist】

- Resist: SU8-3025
- Resist Thickness: 20 μm
- Exposure dose amount: 200 mJ/cm²
- Resist removal: ashing using O_2 plasma

Figures 1 and 2 show the example of photomask pattern and fabricated microstructures observed by using optical microscope, respectively.

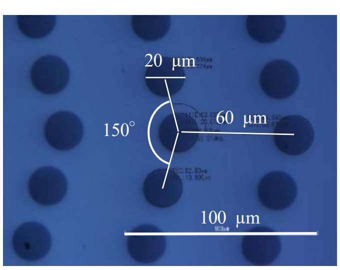

Fig. 1 The shape of the circular holes in the mask that caught our attention

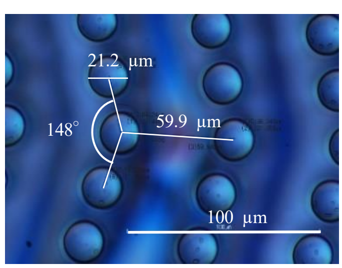

Fig. 2 Example of processed surface with micro cylindrical shapes of a silicon substrate after photolithography

2.2 Hydrophilicity Evaluation Method

The reactive gas used in this RIE procedure was SF_6, CF_4 and O_2.

In the hydrophilicity evaluation test, droplets were placed on the surface of the fabricated microstructures, and the contact angle of the droplets was measured using a contact angle meter. Various factors, such as room temperature, humidity, substrate surface temperature, and droplet temperature, were controlled to ensure consistency in the measurement environment as much as possible. In this study, the droplet volume was set to 0.2 μl, and three measurements were taken for each microstructure, with the average value reported as the result. After each measurement, the droplets were removed from the microstructures using a nitrogen blow, followed by heating on a hot plate set at 110 ℃ and cooling to room temperature for approximately 5 minutes to restore the sample to a measurable state.

Testing Environment:

- Room temperature: 21.5 ℃
- Humidity: 62 %
- Air pressure: 985 hPa

3. Experimental results in Si substrate

3.1 Etching conditions

The etching conditions were adjusted according to the following parameters:

- Acceleration voltage
- Etching gas
- Gas pressure
- Gas flow rate

The reactive gas used in this procedure was SF_6. Table 1 shows the various etching conditions.

Table 1 Etching experimental conditions

	RF power[W]	Flow rate [SCCM]	Pressure [Pa]	Time [min]
No.01	100	30	40	20
No.02	150	30	40	20
No.03	200	30	40	20
No.04	250	30	40	20
No.05	250	30	13.3	20
No.06	250	30	6.7	20

3.2 Hydrophilicity Evaluation results

Table 2 shows the results of measurement contact angle for each of these conditions.

Table 2 Contact angle measurement results

Microstructure number	Average value of contact angle [°]
No.01	15.4
No.02	14.3
No.03	8.6
No.04	7.5
No.05	13.2
No.06	14.4
No.04 no structure	56.3

2.1.3 Results of Etching and Hydrophilicity Evaluation

Figures 3 through 8 show the cross-sectional shapes observed by using SEM for each etching condition. Figures 9 and 10 show the droplet behavior on the microstructure respectively. During observation, the conditions were set to an acceleration voltage of 10 kV and a spot size of 2100 to suppress the effects of charge-up.

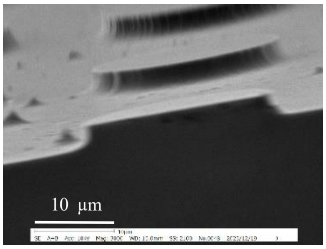

Fig. 3 Cross-sectional shape of microstructure (No.01)

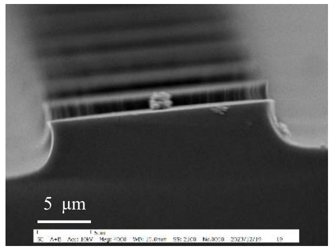

Fig. 4 Cross-sectional shape of microstructure (No.02)

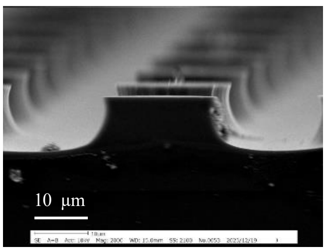

Fig. 5 Cross-sectional shape of microstructure (No.03)

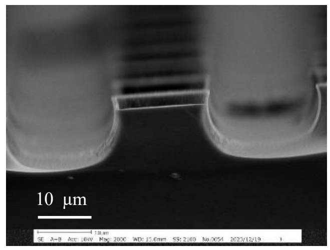

Fig. 6 Cross-sectional shape of microstructure (No.04)

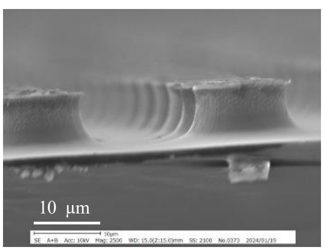

Fig. 7 Cross-sectional shape of microstructure (No.05)

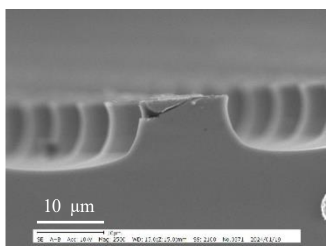

Fig. 8 Cross-sectional shape of microstructure (No.06)

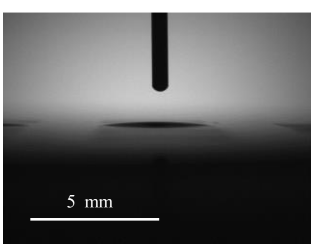

Fig. 9 Droplet during contact angle measurement (No.04)

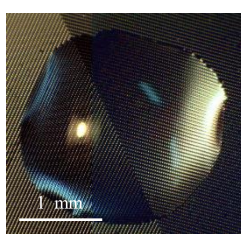

Fig. 10 Droplet viewed from directly above (No.04)

4. Experimental results in Glass substrate

4.1 Fabrication of Microstructures on Glass Substrates

Based on the results from Section 3, the structure that exhibited high hydrophilicity was selected for microstructure on a glass substrate.

Special attention was given to the exposure dose for the glass substrate. According to previous research, the exposure dose for the resist on the glass substrate was set at 1.5 times that in case of the silicon substrate, at 300 mJ/cm² [13]. Other fabrication steps are identical to those outlined in Section 2.1.

4.2 Results of Etching and Hydrophilicity Evaluation

To identify optimal etching conditions, the conditions were determined based on the results from in case of Silicon substrate and previous research findings [14]. The glass substrate fabricated under the same conditions as No. 04 from the silicon substrate etching, which yielded high hydrophilicity, is labeled as No. 07. The conditions derived from prior research are labeled as No. 08 [14]. In case of No. 08, CF_4 and O_2 were used as reactive gases for RIE.

Table 3 shows the various etching conditions for grass etching, while Table 4 shows the results of measurements contact angle for each of these conditions. Figures 11 and 12 show the structures observed by using SEM for each etching condition. Figures 13 and 14 depict the droplet behavior on the microstructures, measurements, respectively.

Table 3 Etching experimental conditions

	RF power[W]	Flowrate [SCCM]	Pressure [Pa]	Time [min]
No.07	250	SF_6:30	40	20
No.08	100	CF_4:20 O_2:8	4	20

Table 4 Contact angle measurement results

Microstructure number	Average value of contact angle [°]
No.07	7.8
No.08	41.0
No.04 no structure	56.3
No.07 no structure	33.8
No.08 no structure	68.2

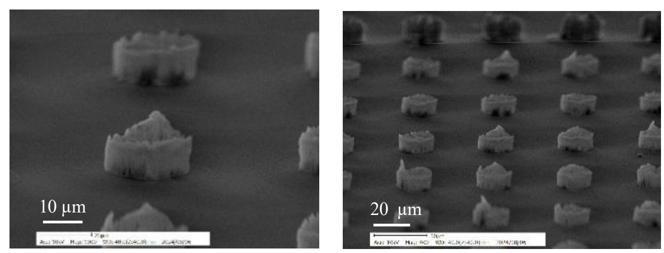

Fig. 11 Glass substrate microstructure (No.07)

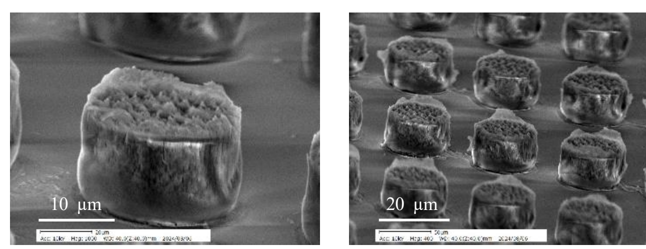

Fig. 12 Glass substrate microstructure (No.08)

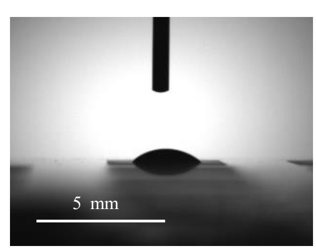

Fig. 13 Droplet during contact angle measurement (No.08)

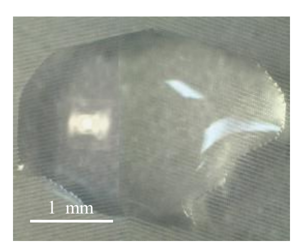

Fig. 14 Droplet viewed from directly above (No.08)

5. Discussions

In case of Si substrate, several factors can be considered to have contributed to the measurement of contact angles indicating excellent hydrophilicity. Firstly, it is likely that the phenomenon known as "pinning " did not occur. This phenomenon involves air trapped within the grooves of microstructures, which can influence wettability. In particular, maintaining a stable air layer beneath a droplet can result in sustained hydrophobicity [15]. In this study, the introduction of an inclination in the recesses likely facilitated the infiltration of liquid into the grooves, thereby minimizing the impact of the pinning phenomenon. In addition, the effects of undercutting during the etching process may also be considered. In cases of significant undercutting, the replacement of air by the infiltrating liquid can become difficult. The curved regions formed by undercutting can impede air flow, preventing proper replacement. It is therefore expected that etching under appropriate pressure can produce structures with minimal undercutting, resulting in improved hydrophilicity.

In case of glass, the etching conditions are identical for No. 04 (Si) and No. 07 (SiO_2), the structural shapes differ significantly, as evident from Figures 6 and 11. The silicon substrate exhibits a sloped structure due to isotropic etching, while such a shape is not observed in the glass substrate. Additionally, although the contact angle measurement for No. 07 indicates a high degree of hydrophilicity, the structure is degraded, suggesting that the result cannot be attributed solely to the microstructural shape. The significant difference in etching effects can be attributed to the differing crystal structures.

Regarding No. 08, as shown in Figure 12, while a sloped structure is not present, a cylindrical shape was successfully formed. The contact angle measurement yielded a value of 41.0°, indicating hydrophilicity. However, due to the different shape of the microstructures fabricated on the glass substrate compared to those on the silicon substrate in this study, it is not possible to definitively determine the hydrophilic properties of the glass substrate. It is necessary to reconsider the method of fabricating cylindrical shapes with slopes, similar to the shapes on the silicon substrate. One approach could be, as emphasised in Section 3.1, to first observe the differences caused by the acceleration voltage. Moreover, noticeable contamination, such as residual resist agent, was observed on the structure's surface. Therefore, the ashing method should be re-evaluated. It may be beneficial to explore alternative methods, such as using solutions to strip the resist agent, to determine an optimal ashing method for glass substrates.

6. Conclusions

Based on the findings from section 3, where excellent etching conditions for achieving high hydrophilicity were obtained, it is necessary to use these conditions as a standard, consider many other conditions, and investigate the effects of parameters other than pressure and output values. Additionally, as discussed in the previous section, the underlying reasons for the observed high hydrophilicity should be clarified by examining the changes within the structural grooves when a liquid is applied.

Although section 4 did not yield particularly useful results, it laid the groundwork for fabricating microstructures on glass substrates via dry etching. Directly applying the research findings from silicon substrates to glass substrates is challenging. Initially, establishing appropriate conditions and increasing the number of samples will help elucidate the similarities and differences compared to silicon substrates.

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