Water harvesting capability of petal-effect hafnia films and hydrophilic-hydrophobic patterned films

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Two types of petal-effect hafnia films and hydrophilic-hydrophobic stripe-patterned films consisting of 1-mm-wide lines and spaces were fabricated and their water harvesting capability was investigated. Petal-effect hafnia films containing glycine and glycolic acid were prepared by a sol-gel technique. Hydrophilic-hydrophobic stripe-patterned films were fabricated by screen printing a hydrophobic hafnia sol as a paste onto a superhydrophilic alumina film substrate. The water harvesting capability of the films was evaluated using a custom-built water collecting apparatus. The mass of water both on the sample surface and in a petri dish set under the sample was measured to evaluate the water collecting capability. When a vapor covered the petal-effect film, small dew droplets formed on the surface and grew to large hemispheric ones, but most of the water remained on the sample surface without falling into the petri dish. When a vapor covered the patterned film surface, small droplets and large, long ones formed on the hydrophobic and hydrophilic patterns, respectively. The large droplets that grew on the hydrophilic patterns fell into the petri dish. The total amount of water that collected on the petal-effect and the patterned films was ca. 1.6 times larger than the respective amount collected with a superhydrophilic alumina film, a hydrophobic hafnia film and a glass substrate as a control reference. The patterned films collected a larger amount of water in the petri dish than the petal-effect films did because the hydrophilic molecules of organic acids on the surface of the latter films retained a larger amount of droplets. It is concluded that both the petal-effect films and the patterned films have superior water harvesting capability from a vapor in the ambient atmosphere.

Key-words: Water harvesting, Hydrophilicity, Hydrophobicity, Patterned film, Petal effect, Screen printing

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1. Introduction

Dry and arid areas represent a frontier for humankind to live and expand the range of human activity. Water harvesting devices from dew or fog are needed because a sufficient supply of drinking water is an essential item for life and activity in such regions. To live in an arid region, several plants and animals, for example, dune bushman grass (Stipagrostis sabulicola) and the Namib Desert beetle Stenocara gracilipes, have adapted different strategies for harvesting water from a foggy atmosphere.\(^{1-3}\) The beetle harvests water on its back from early-morning fog, drinks it and lives on. The beetle’s back consists of hydrophilic bumps on a hydrophobic surface.

Several surfaces and films inspired by the beetle’s back have been artificially prepared.\(^{4-9}\) All the reported surfaces and films have micro-scale hydrophilic spots surrounded by a hydrophobic background. For example, hydrophilic spots of 750 \(\mu\)m in diameter were prepared on a superhydrophobic surface\(^9\) and superhydrophilic circles of 500 \(\mu\)m in diameter and spaced at 1 mm intervals were fabricated on a hydrophobic background.\(^9\) The water collecting capability of the samples was investigated under a condition of a cooled sample surface in a humid atmosphere.\(^5\)

Recently, petal-effect films with both superhydrophobicity and high adherence of water droplets have been reported.\(^{10}\) Feng et al.\(^{10}\) reported that the petals of red roses and polyvinyl alcohol (PVA) films with an inverse petal structure had a microstructure with a surface roughness of a few micrometers and showed superhydrophobicity and a high adhesive force with water.

One of the authors reported that sol–gel-derived hafnia films containing glycolic acid with a flat surface showed the petal effect and that the effect was ascribable to the pinning effect of hydrophilic groups of glycolic acids on the hydrophobic surface of hafnia.\(^{11}\)

On the basis of these findings, it is inferred that water harvesting devices must have both hydrophilic and hydrophobic areas, but the areas can have several different morphologies and shapes. It is reasonable to think that a petal-effect hafnia film should have a water harvesting capability because it has molecular-sized hydrophilic spots of organic acids surrounded by a hydrophobic background with a flat surface. We have designed a new type of water harvesting device that has a pattern of hydrophilic and hydrophobic stripes.

The purpose of this work is to prepare and evaluate the water harvesting capability of petal-effect films with a flat surface and hydrophilic-hydrophobic stripe-patterned films. Petal-effect films were prepared by a sol–gel technique using two organic acids of glycolic acid and glycine. Stripe-patterned films were prepared using a common, low-cost screen printing technique.

2. Experimental procedure

2.1 Preparation of petal-effect hafnia films A and B

Hafnium chloride (5.44 g) was dissolved in H\(_2\)O (32 g) in a N\(_2\) atmosphere. To the solution, 29% aqueous ammonia (9 mL) was added to precipitate hafnium hydroxide, and the precipitate was washed with water to a level of pH 7 of the filtrate. To the

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precipitate, a mixture of H$_2$O (32.0 g) and 35% hydrochloric acid (4.20 g) was added, followed by heating at 80–82°C for 3 h. The weight of the solution was adjusted to 80 g by adding H$_2$O. To the solution, a 1.9% glycol acid solution (8.42 g) or a 10% glycine solution (1.60 g) was added and stirred at ambient temperature for 2 min to obtain hafnia sols A and B, respectively. Sols A and B were then coated on alkali-free glass substrates (AF-45, Schott), followed by application of ultraviolet (UV) irradiation to the films for 10 min using a high-pressure mercury lamp (H1000L, Toshiba Lighting & Technology Corp.) to obtain transparent hafnia sols A and B.

Hafnia gel powders A and B were obtained by evaporating hafnia sols A and B with a rotary evaporator.

2.2 Preparation of hydrophilic-hydrophobic stripe-patterned films

Superhydrophilic alumina films were prepared as follows. A mixed solution of a nanofiber (ca. 4 nm in diameter and 1400 nm in length) alumina sol (1.0 g) and H$_2$O (19.0 g) adjusted to a pH of 1 with HCl was spray-coated on alkali-free glass substrates (AF-45, Schott) and fired at 500°C for 30 min to obtain alunina films. The films were hydrothermally treated as follows to obtain superhydrophilic surfaces. The films (50 mm × 25 mm) were dipped in 1 wt% nitrilotris(methyleneephosphonic acid) (NMP) aqueous solutions (80 mL) that were heated in autoclaves at 180°C for 6 h to impart superhydrophilicity to the films. The films were then washed with water and dried in air.

Hydrophobic hafnia sol C for obtaining a hydrophobic pattern was prepared as follows. To the hafnium hydroxide mentioned above, 99.7% acetic acid (30.0 g) was added, followed by heating at 80–82°C for 3 h. Hafnia sol C was obtained by adding H$_2$O to adjust the weight of the solution to 20 g. Transparent hydrophobic hafnia films C were prepared by coating the sol on alkali-free glass substrates (AF-45, Schott), followed by application of UV irradiation to the films for 10 min using a high-pressure mercury lamp (H1000L, Toshiba Lighting & Technology Corp.).

Hydrophilic-hydrophobic patterned films were prepared using a screen printing machine (DP-320, Newlong Seimitu Kogyo) as follows. A paste of hafnia sol C was screen-printed on substrates of superhydrophilic alumina films (5 cm × 2.5 cm). A polyester screen with a patterned area of 5 cm × 2.5 cm and with 380 meshes per inch and a 4-μm-diameter thread were used in the printing process. Open spaces and 1.0-mm-wide closed stripe patterns were adopted to print patterns of 1.0-mm-wide lines and spaces. The superhydrophilic alumina film was mounted in the printing machine at a distance of 2.4 mm from the screen plate. Hafnia sol C (viscosity of 3.0 mPa·s and weight of ca. 1.8 g) was spread at the edge of the screen pattern. A rubber squeegee with an angle of 70° was drawn over the screen at a printing pressure of 0.20 MPa and a speed of 300 mm/s. Stripe patterns of hydrophobic hafnia were printed onto the superhydrophilic alumina film. The printed samples were cured at 200°C for 30 min.

2.3 Measurements

The surface components of the films and the compositions of the powder samples were evaluated by Fourier transform infrared (reflection absorption) spectroscopy [FT-IR(RAS)] and FT-IR spectroscopy, respectively, using a PerkinElmer Spectrum One spectrometer. The surface morphology and cross-sectional images of the patterned films were evaluated by field-emission scanning electron microscopy (FE-SEM) using a JEOL JSM-6500F. The viscosity of the hafnia sol was measured with a Toki Sangyo viscometer BMII at 25°C. The contact angle of water droplets on the films was measured using 2-μL water droplets and the sliding angle was measured using 50-μL water droplets. Measurements were made with an automatic Kyowa DM-501 contact angle meter. Contact angles and sliding angles were measured at five different points for each sample and averaged. The maximum amount of water droplets adhering to a sample surface was evaluated as follows. A sample was inclined at 30° or 90° (a vertical position). A certain amount of water was put on the sample surface using a microsyringe. The mass of the droplets was increased until the droplets began slipping. The maximum amount of water adhering to the surface was determined at that moment.

The maximum amount of water droplets adhering to the sample surface when turned upside down was also evaluated as follows. A sample with a certain amount of water droplets on the surface was inclined from 0° (a horizontal position) to 90° (a vertical position) and then 180° (the film surface was turned upside down). The maximum amount of water adhering to the surface was determined at that moment. The surface roughness (R$_s$) of the films was measured by atomic force microscopy (AFM) using a Digital Instruments NanoScope 3a controller. The water harvesting capability of the samples was evaluated with a custom-built water collecting apparatus illustrated in Fig. 1 as a water harvesting model. Water vapor was generated from a heated water bath. Dew droplets formed on the sample and glass surfaces and fell into petri dishes. The apparatus was surrounded with acrylic film to prevent vapor diffusion from the apparatus.

![Fig. 1. Water harvesting apparatus used in this study.](image)
The results are shown in Table 1. The contact angles of water droplets on the films were 87° (average) ± 2.7° (standard deviation) − 90° ± 1.0°, indicating that the films were hydrophobic. Films A and B retained a large amount of water of 24 μL ± 1.6 μL and 25 μL ± 1.1 μL, respectively, when the films were inclined to 90 and 180° (turned upside down). The maximum values on the sample surfaces were the same for both 90 and 180°. However, hydrophobic hafnia film C did not retain 20 μL of droplets under the same conditions.

These results indicate that the hafnia film containing glycine and with a flat surface showed the petal effect, as did the film containing glycolic acid.\(^{11}\)

### 3. Results and discussion

#### 3.1 Films

##### 3.1.1 Petal-effect hafnia films

The FT-IR spectra of the hafnia gel powders A and B were measured to identify the film components and the results are shown in Fig. 2. The spectra of the former and the latter showed absorbance at 1611 and 1607 cm\(^{-1}\), respectively, which was ascribed to the COO\(^{-}\) group of organic acids.\(^{12}\) The absorbance at 1486 cm\(^{-1}\) of hafnia gel B was ascribed to the NH\(_2\) group of glycine.\(^{12}\) These results indicate that hafnia films A and B contained glycolic acid and glycine, respectively.

The surface morphology of hafnia films A and B was evaluated by FE-SEM and the results are shown in Fig. 3. Both films had flat, uniform surfaces without any micro- or nano-structures, whereas the surfaces of the petal-effect films reported in reference 10) had micro-structures of micropapillae 16 μm in diameter and 7 μm in height. The surface roughness (\(R_s\)) of film A measured by AFM was 1.4 nm (average) ±0.3 nm (standard deviation), indicating that the film surface was homogenous and that the effect of roughness on wetting could be ignored.\(^{13}\)

#### 3.1.2 Superhydrophilic alumina film and hydrophobic hafnia film C

The preparation procedure and properties of the superhydrophilic alumina film were detailed in a paper submitted to this journal previously.\(^{14}\) The contact angle of water droplets on the film was 8° ± 1.0°, indicating that the film was superhydrophilic. FE-SEM observation of the surface revealed a micro-structure with a serrated morphology.

The contact angle of water droplets on hafnia film C was 97° ± 2.0°, indicating that the film was hydrophobic. FE-SEM observation of the film revealed that the surface was flat and uniform. The FT-IR(RAS) spectrum of the film showed absorbance at 1452 cm\(^{-1}\) ascribed to the CH\(_3\) group,\(^{15}\) indicating that the CH\(_3\) group of acetic acid was present at the film surface.

#### 3.2 Hydrophilic-hydrophobic patterned film

The hydrophilic-hydrophobic patterned film was fabricated by a screen printing technique. A low viscous hafnia sol of 3.0 mPa·s in viscosity was successfully printed on a superhydrophilic alumina film via a screen with a striped pattern of 1-mm-wide lines and spaces. Following printing, the hydrophobic hafnia and hydrophilic alumina patterns were obtained on a glass substrate. The pattern morphology was evaluated with an optical microscope and FE-SEM. The optical microscope observation (Fig. 4) revealed that the hydrophobic pattern was flat, continuous and crack-free.

An FE-SEM image of the surface of the hydrophobic pattern [Fig. 5(a)] showed that it was flat and continuous, whereas the surface of the hydrophilic pattern [Fig. 5(b)] exhibited a micro-structure with a serrated morphology. A cross-sectional image of the hydrophilic pattern [Fig. 5(d)] revealed one layer (B) with irregular particles on the substrate (C) and a thickness of 0.2 μm. A cross-sectional image of the hydrophobic pattern [Fig. 5(e)] showed two layers on the substrate (C), i.e., a top layer (A) of hydrophobic hafnia with a flat morphology and a thickness of 0.3 μm and an under-layer (B) of hydrophilic alumina which was the same as layer (B) of the film in Fig. 5(d).

The line width reproducibility of the patterns was evaluated by measuring line widths in the central area of five hydrophobic patterns with a micrometer and averaging them. It was also evaluated by measuring five points of the central pattern and...
averaging the values. The line widths measured by both methods were 1.00 mm (average) ± 0.01 mm (standard deviation), indicating that the patterns showed superior line width reproducibility.

In general, the paste used in screen printing has high viscosity (0.1–500 Pa s). However, in this study, the printing of the low viscous hafnia sol produced flat, continuous hydrophobic patterns that showed excellent line width reproducibility. When hafnia sol C was screen-printed on an alumina film with a flat surface prior to the hydrothermal treatment, the patterns obtained showed a discontinuous, island-like structure and a narrow line width because the alumina film repelled the hafnia sol. It is inferred that the uniform coating of low viscous hafnia sol C on the superhydrophobic alumina film was due to superhydrophilicity and the micro-structured surface morphology, resulting in the formation of flat, uniform patterns with superior line width reproducibility.

Water droplet contact angles and sliding angles on the patterned film were measured. When a water droplet was put on the patterned film, it moved from the hydrophobic area to the hydrophilic area and spread to form a long droplet because of the small zigzag line morphology of the hydrophobic pattern. The contact angles of the water droplet (2 μL) vertical and parallel to a line were 81° ± 2° and 38° ± 1°, respectively. The sliding angle of the water droplet (50 μL) parallel to the line was 14° ± 1° and the droplet did not slip vertical to the line even when the droplet was inclined to 90°, indicating that water droplets slide easily when parallel to the lines.

The surface roughness (Ra) values of the hydrophobic and hydrophilic areas measured by AFM were 1.0 nm ± 0.1 nm and 14 nm ± 4 nm, respectively. These values coincided with the FE-SEM results, indicating that the hydrophobic area was homogeneous like the petal-effect films.13

Wetting behavior of water on micro-stripe-patterned films has been actively studied.16–18 Morita et al.19 reported macroscopic anisotropy of wetting on patterned films. They prepared stripe-patterned films with a line width of 1–20 μm. The contact and sliding angles on the film surfaces showed anisotropic wetting; the angles vertical to a line were large, whereas those parallel to a line were small. These results coincide with our findings.

3.3 Water harvesting

The water harvesting capability of the petal-effect hafnia films containing organic acids and the patterned film of 5 cm × 5 cm in size was evaluated for 2 h under a condition of 100% RH at 47°C using the custom-built water collecting apparatus. The mass of water collected both on the sample surface and in the petri dish

![Fig. 4. Optical microscope photograph of hydrophobic and hydrophilic patterns of hydrophilic-hydrophobic patterned film (×50).](a)

![Fig. 5. FE-SEM surface images of (a) hydrophobic pattern and (b) hydrophilic pattern of hydrophilic-hydrophobic patterned film (×50,000). FE-SEM cross-sectional images of (c) hydrophobic pattern on hydrophilic film and (d) hydrophilic film of hydrophilic-hydrophobic patterned film (×50,000). A, B and C denote hydrophobic pattern, hydrophilic film and glass substrate, respectively.](b)
was measured. The water harvesting capability of the superhydrophilic alumina film and hydrophobic hafnia film C was also evaluated in the same condition. Each experimental condition was almost the same because the glass substrate used as a control reference collected almost the same amount of water of 0.30 g (average) ± 0.04 g (standard deviation).

When a vapor covered the petal-effect hafnia films in the apparatus, the transparent film surfaces immediately became opaque, followed by the formation of small droplets that grew to large hemispheric shapes. A photograph of the film containing glycolic acid after 1 h of the water harvesting process (Fig. 6) showed a large amount of water droplets on the surface. A small number of droplets slid to the bottom of the film and fell into the petri dish with time.

On the other hand, when a vapor covered the stripe-patterned film surface, the transparent hydrophobic areas immediately became opaque, but the hydrophilic areas apparently remained transparent. After 1 h, small water droplets and large, long ones formed on the hydrophobic and hydrophilic patterns, respectively (Fig. 7). Hong et al.\(^5\) reported that small dew droplets formed on a hydrophobic surface grew to a certain value (ca. 10 \(\mu\)L) and moved toward a hydrophilic area. In this study, movement of the droplets from the hydrophobic patterns was not clearly observed. However, droplets on the hydrophobic patterns were presumed to move to the hydrophilic ones. The large droplets on the hydrophilic patterns slid to the bottom of the film and then fell into the petri dish with time.

When a vapor covered hydrophobic hafnia film C, the surface became opaque like that of the petal-effect films and hydrophobic patterns and small droplets formed. However, unlike the petal-effect films and the patterned film, the small droplets did not grow and did not fall into the petri dish because their size remained constant during the experiment. In the case of the superhydrophilic alumina film, a water film formed on its surface in a vapor and large droplets formed at the bottom of the film with time, which then fell into the petri dish.

The mass of the water collected on the sample surfaces and in the petri dishes and the total amount are given in Table 2. The patterned film and the petal-effect films collected a large and almost equal total amount of water. However, the superhydrophilic and the hydrophobic films collected a smaller total amount of water, as did the glass substrate. The total amount of water collected with the petal-effect films and patterned film was ca. 1.6 times larger than that for the superhydrophilic film, the hydrophobic film and the glass substrate, indicating that the petal-effect films and patterned film were able to harvest more water from the vapor in the ambient atmosphere.

The petal-effect films collected 4.2–5 times more water on their surfaces than the amount in the petri dishes, whereas the patterned film collected almost the same amount of water both on the surface and in the dish. Lee et al.\(^3\) prepared a spot-patterned film consisting of superhydrophilic spots of 500 \(\mu\)m in diameter surrounded by a superhydrophobic background. They reported that a surface cooled to 10.0\(^\circ\)C in a humid atmosphere at 25\(^\circ\)C collected water and the water dropped into a container set under the film.\(^3\) The film surface was reported to collect ca. 8 times more water than the container did.\(^3\) This report and our results indicate that the petal-effect and hydrophilic spot-patterned films collected a lot of water, but almost all of it remained on the sample surface without falling off. The reason is that water adhered to the petal-effect films by the pinning effect of the hydrophilic groups of organic acids\(^7\) or adhered to the micron-
size hydrophilic spots by the hydrogen bonding of the hydrophilic groups on the spots.

The petal-effect films and the stripe-patterned film showed different types of water harvesting. The films collected almost the same total amount of water. However, the amounts of water collected in the petri dishes with the petal-effect films and the patterned film were 0.07 g ± 0.06 g – 0.09 g ± 0.04 g and 0.25 g ± 0.11 g, respectively. The patterned film collected 2.8–3.6 times more water than the petal-effect films did.

To identify the difference in the two types of water harvesting, the maximum amount of water adhering to the film surfaces inclined to 30° was measured. The petal-effect films retained 57 μL (average) ± 4.7 μL (standard deviation) of water whereas the hydrophilic pattern of the patterned film retained 27 μL ± 4.7 μL. These results indicate that a large amount of water adhered to the petal-effect films due to the pinning effect, resulting in the retention of a lot of water on the surface.

4. Conclusions

Petal-effect hafnia films and hydrophilic-hydrophobic stripe-patterned films were fabricated and their water harvesting capability was investigated. Hafnia films containing glycolic acid and glycerol were prepared by a sol–gel method and they showed the petal effect. The patterned film was fabricated by a screen printing technique using a hydrophobic hafnia sol containing acetic acid as a paste and a superhydrophilic alumina film as a substrate. The hydrophobic patterns had flat, continuous surfaces and the hydrophilic ones had a micro-structure with a serrated morphology. The patterns showed excellent line reproducibility. The water harvesting capability of the films was evaluated using a custom-built water collecting apparatus. When a vapor covered the petal-effect hafnia films, small droplets formed on the surface and grew to large hemispheric shapes. A small amount of droplets fell into a petri dish. When a vapor covered the patterned film surface, small droplets and large, long droplets formed on the hydrophobic and hydrophilic patterns, respectively. The large droplets on the hydrophilic patterns fell into the petri dish. The amount of water collected on the film surfaces and in the petri dishes was measured. The petal-effect films and the patterned film collected ca. 1.6 times more water than the hydrophobic film, the superhydrophilic film and the glass substrate, indicating that the petal-effect films and the patterned film have the capability to harvest water from a vapor in the ambient atmosphere.

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