

# HIGHLY REPRODUCIBLE AND SCALABLE TRANSPARENT PDMS THIN FILM WITH SUPER-HYDROPHOBIC SURFACE

J.H. Park<sup>1</sup> and D.W. Lee<sup>1\*</sup>

<sup>1</sup>Department of Mechanical Engineering, Chonnam National University, Gwangju, SOUTH KOREA

## ABSTRACT

This paper describes a simple method of making an optically transparent super-hydrophobic PDMS thin film by using a reusable photo-curable polymer mold. A photoresist mold is prepared using underexposed and under-baked positive photoresist (PR), which create unique hierarchical micro/nano structures. The reverse image of the PR mold is replicated to a PDMS substrate on its surface. The patterns of replicated mold is transferred again to the photo-curable polymer using a home-made UV exposure system. The photo-curable polymer mold is very suitable for the use in a roll-to-roll system for mass production of the film. Nano-silica powder with hydrophobicity is additionally sprayed on the micro/nano structured PDMS surface for further improvement of the hydrophobicity, which slightly decrease the transparency of the film. The fabricated PDMS thin films with hierarchical micro-/nano-scale surface texturing show water contact angle of 150° or greater. Optical transmittance within the range of visible light of wavelengths between 400 and 800 nanometers is experimentally confirmed using a spectrophotometer. High optical transparency of the super-hydrophobic PDMS film is also confirmed on solar panels.

## INTRODUCTION

Super-hydrophobic surfaces have the characteristics of highly hydrophobic, i.e. extremely difficult to wet. In general, the contact angles of a water droplet is greater than 150° and the roll-off angle is less than 10° on the hydrophobic surface [1]. Inspired by such amazing natural wonders, there have been tremendous efforts to create artificial super-hydrophobic surfaces with water contact angles greater than 150° for applications such as self-cleaning, antisticking, and drag reduction applications.

It was found that a hierarchical dual micro-/nano-scale structure design is an effective way to create super-hydrophobic surfaces [2-4]. Various materials such as silicon, polymer, and carbon nanotubes have been studied to make a hierarchical micro-/nano-structured surface such as lotus leaf [5-7]. However, those ideas still suffer from some technical issues such as transparency, scalability, manufacturing cost, flexibility etc. In order for surfaces to be optically transparent, the material of films should be inherently transparent as well as the surface roughness should be smaller than the wave length of visible light. Polymer such as poly-methylmethacrylate (PMMA), polystyrene (PS), polydimethyl-siloxane (PDMS) have been widely investigated for the applications that requires high optical transparency. One-step fabrication of optically transparent PDMS film is also reported in our previous report [8]. The unique PDMS structures are greatly improved the hydrophobicity, however, it is not able to reuse due to the use of a thick photoresist as a mold structure.

The main objective of this research is to report a novel method of an optically transparent super-hydrophobic thin film to overcome drawbacks of currently available fabrication methods. We employ a negative photoresist mold with micro/nano-sized structure such as lotus leaves through an easy and simple photolithography process. The unique structures are transferred to the PDMS surface and the structure are retransferred to a photo-curable polymer layer. The reusability of the photo-curable polymer is very suitable for mass production processes such as a roll-to-roll or a roll-to-plate. The hydrophobicity of the fabricated PDMS thin film from the reusable mold is greatly improved in comparing with a normal PDMS thin film. The new fabrication process and successful experimental results reveal that the proposed idea has significant potential for diverse use of the super-hydrophobic transparent PDMS thin film.

## EXPERIMENTAL METHODS

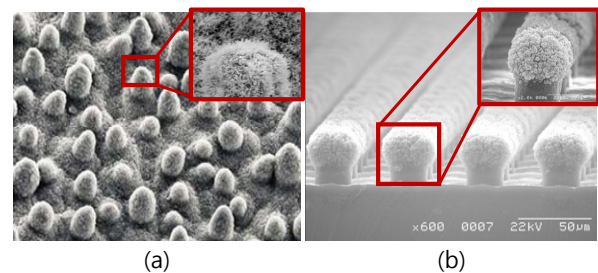


Figure 1 SEM images for natural Lotus leaf (left) and the fabricated micro/nano structured PDMS (right). The lotus leaf has a micro-sized protrusion, and its micro-sized structure also has a unique structure with nano-sized protrusions. The surface shape of the film also has a nano-sized structure and a micro-sized structure similar to a lotus leaf.

Figure 1 shows photographs of real (nature) and artificial (proposed) lotus leaf. The hierarchical structures of the lotus leaf are formed out of a characteristic epidermis and the covering waxes. The epidermis of the lotus plant possesses papillae with 10 µm to 20 µm in height and 10 µm to 15 µm in width as shown in Fig 1 (a). The surface of epidermis with microstructures are covered with epicuticular waxes. These superimposed waxes are hydrophobic and form the second layer of the hierarchically double-layered structure. The unique double structures of the lotus leaf are successfully mimicked using a photoresist and a reusable polymer molds. In a conventional photolithography, it is strongly desirable to have a vertical side wall during the exposure and development processes. Here, we hypothesized that under soft-baking condition combined with under exposure creates unexpected patterns which is undesirable in the conventional photolithography. However, the unique

negative patterns of PR is relatively useful for super-hydrophobic applications once the shapes are transferred to the PDMS as shown in Fig 1 (b). The high surface tension of water causes droplets to assume a nearly spherical shape, since a sphere has minimal surface area, and this shape therefore demands least solid-liquid surface energy. On contact with a surface, adhesion forces result in wetting of the surface. Either complete or incomplete wetting may occur depending on the structure of the surface and the fluid tension of the droplet. Additionally, the hydrophobic water-repellent hierarchical structures of the PDMS surface also cause self-cleaning effects, which behavior is very attractive in engineering applications.

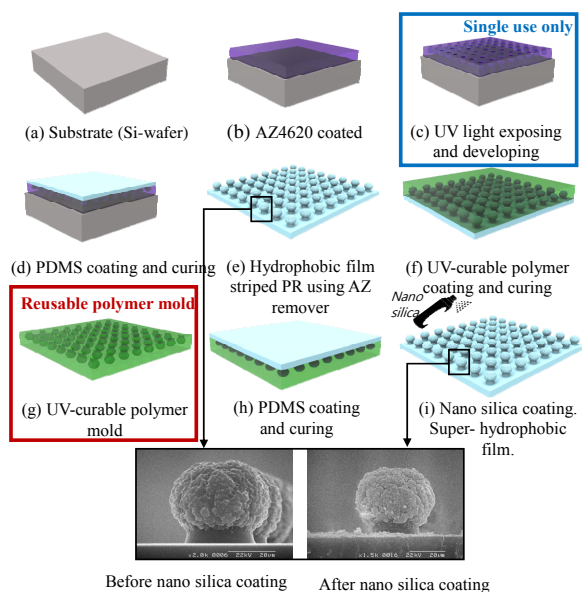


Figure 2. Schematic of fabrication process and SEM micrographs shows the fabricated micro/nano structured PDMS before and after nano silica coating

A process flow for the fabrication of optically transparent super-hydrophobic PDMS thin films is shown in Fig. 2. The thick AZ4620 photoresist is multi-coated on a 4-inch silicon wafer (Fig. 2b). Underexposed and under-baked positive photoresist technique is employed to create the reverse image of hierarchical micro/nano structures (Fig. 2c). The prepared PR mold with negative structures is covered with by PDMS (Base: curing agent = 10: 1). The sample is then de-gassed under a low vacuum condition until trapped bubbles are completely removed from interface between PDMS and PR mold (Fig. 2d). Next, the PDMS layer is cured above 80°C for 4h. Finally, super-hydrophobic PDMS film is replicated by removing the PR mold with an acetone solution (Fig. 2e). To optimize under soft-baking and under exposure processes various temperature and exposure time are employed during the basic experiments. After that, the UV-curable polymer with a liquid phase is poured on the replicated PDMS film with unique structures on the surface (Fig. 2f). Next, the UV-curable polymer is solidified by a home-made exposure system (Fig. 2g) and is then separated from the replicated PDMS mold (Fig. 2h). The fabricated UV-curable polymer mold is very useful for repeatable production of the super-hydrophobic PDMS

thin film. Nano-silica is then sprayed on the PDMS surface (Fig. 2i). Figure 2 also shows SEM images of replicated optically transparent super-hydrophobic PDMS films with and without additional nano-silica coating processes.

One of great advantages of the proposed fabrication method is the use of reusable and scalable polymer mold. It also doesn't require any additional chemical treatment for easy separation of the cured PDMS film from the UV-cured polymer mold with negative structures. A tiny mechanical force is enough while detaching the PDMS film from the mold. The hydrophobic characteristics is also greatly improved by employing additional nanoparticles on the replicated PDMS thin film.

#### (a) SOFT PR MOLD FOR SINGLE USE

The unique shape of the PR mold for single use is optimized by controlling the baking time of the positive photoresist (AZ4620). The fabricated PR mold is made by stacking a total of three AZ4620 positive photoresist layers on a 4-inch Si wafer. After coating the first PR, soft-baking process is performed in a convection of at a temperature of 55 °C for 3 min. The second PR coating is then repeated with the same process condition of that of the first layer. After the third PR coating, the multi-layered PR is soft-baked again in a convection oven at 55 °C for 45 min. Significant under soft-baking process condition allow the thick photoresist to keep certain amount of solvents which enhance the dissolution rate of the PR. In general, the thick PR layer requires an increased soft-baking time when the convection oven is employed for the baking process. When the PR is cured in ovens, solvent starts to evaporate from the PR surface. The cured PR surface layer disturbs continuous evaporation of solvent from the PR. This is due to that the solvents remaining inside the PR is evaporated through the cured PR surface layer. In this way, it is possible to fabricate an artificial Lotus leaf with a negative patterns. This is thanks to the insufficient soft-baking and exposing of the thick PR layer.

#### (b) PDMS POSITIVE MOLD

PDMS is known as optically clear, non-toxic, and non-flammable material. It is also called dimethicone and is one of several types of silicone oil. Water contact angle is close to 100° on a smooth PDMS surface and it can be increased up to 150° when additional processes are performed on the flat PDMS. PDMS component is mixed with a known ratio (Base:curing agent = 10:1) and is placed in a desiccator to de-gas under a vacuum condition. The de-gassed PDMS solution is gently poured on the soft-baked PR mold and then placed in a vacuum oven to duplicate the reverse image of the PR molds. This minimize the introducing bubbles into the PDMS layer and the PDMS solution fully occupied all concave areas of the PR mold. The thickness of the cured PDMS layer is about 2 mm and this is controllable by changing a spin speed and the number of PDMS coating layer. The fabricated PDMS mold is duplicated again to another polymer material (Figure 3a).

#### (c) POLYMER MOLD FOR MULTI-USE

The UV-curable polymer with a liquid phase is poured on the fabricated PDMS mold with unique structures on the

surface and is then solidified by a home-made exposure system. The UV-curable polymer is prepared using 4-Hydroxybutyl acrylate (85%), Acrylic acid (11%), Ethyleneglycol dimethacrylate (1%), 2'-dimethoxy-2-phenyl-acetone phenone (3%). After UV exposure, solidified UV-curable polymer mold is gently peeled off from the duplicated PDMS mold using a tweezer. (Figure 3b). The use of the photo-curable polymer as a mold provides a great advantage in mass production of the optically transparent super-hydrophobic PDMS thin film. This is thanks to the easy separation of the PDMS film from the polymer mold and reusability of the mold material. A process flow for the fabrication of the duplicated PDMS thin film is similar to the method employed in the first PDMS mold fabrication. An optical image of the optically transparent re-replicated PDMS thin film is shown in Fig 3. (c). The size of the super water-repellent PDMS film is about 7 cm  $\times$  7 cm. Water contact angle, light transmittance, self-cleaning effect are systematically investigated using various techniques.

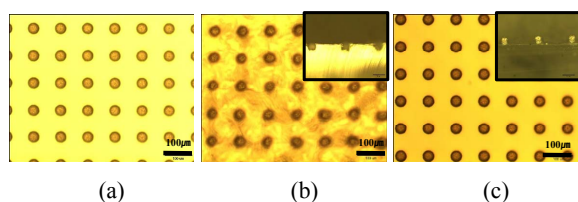


Figure 3. Optical images of (a) hydrophobic PDMS positive mold (b) replicated UV-curable polymer mold (c) re-replicated ultra-hydrophobic film striped from the UV-curable polymer mold

## RESULTS AND DISCUSSION

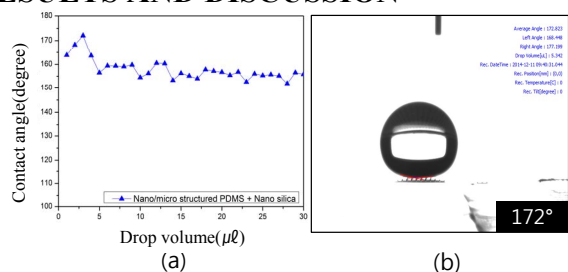


Figure 4. (a) Water contact angle with increasing the amount of water droplet on ultra-hydrophobic PDMS films (b) Optical image showing the maximum water contact angle ( $>172^\circ$ ) on the PDMS film

The super-hydrophobic surface usually has contact angles of a water droplet of greater than  $150^\circ$ . Previous studies have measured the water contact angle value in the amount of about 5  $\mu$ l water [9] but this is insufficient as a basis for water repellency in real life such as a rain shower having different water volumes. For this reason, the water contact angle value is measured by increasing the volume of the water droplet (minimum 1 ~ maximum 30 $\mu$ l). The replicated super-hydrophobic film showed a maximum water contact angle of  $172.82^\circ$  at 3  $\mu$ l and the value of more than  $155^\circ$  are achieved at all different water volumes. This proves that the optically transparent super-hydrophobic film has excellent water repellency. It is also

expected that water repellency will be maintained even in a real rain shower where water droplets of various sizes are present.

### (a) OPTICAL TRANSMITTANCE

In order to evaluate the transparency of PDMS films fabricated using the reusable photo-curable polymer mold, the transmittance in the visible region (400-800 nm) is measured using a UV-Visible spectrometer. Two different types of PDMS films with and without nano-silica are employed in the characterization and the transmittance of the films is compared as shown in Fig 5. In the case of the PDMS film without nano-silica coating, the average transmittance is close to 98.9%. The value is slightly decreased to 95.7% since nano-silica is coated on the PDMS film using a spray method. However, both thin films still show a high light transmittance for practical applications. These results indicate that hierarchical micro/nano structures presented doesn't influence to the optical transparency of the thin film.

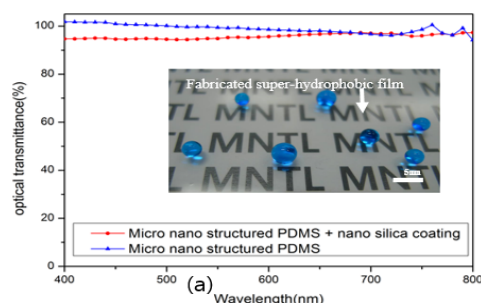


Figure 5. Optical transmittance as a function of wave length for two different PDMS film

### (b) SELF-CLEANING EFFECT

In the case of lotus leaves, it is always clean with only a rain shower. This is called as self-cleaning effect [10]. The duplicated super-hydrophobic film produced also expect to have self-cleaning ability due to the unique structures similar to lotus leaves. The PDMS thin film is placed on top a printed letter of a paper. The PDMS surface is initially contaminated with black dusts (Fig. 6 (a)) and the water droplets are then applied to the PDMS surface using a syringe as shown in Fig. 6 (b). Self-cleaning ability is experimentally confirmed as shown in Fig 6 (c). In the case of contaminants, it is obtained from the filter of a vacuum cleaner. The results also compared with that of a normal PDMS film. It was not able to completely remove the contamination on the flat PDMS surface with only water droplets. Due to the ultra-high hydrophobicity and the self-cleaning effects, the proposed PDMS thin film has a great potential for the use in various industry areas.

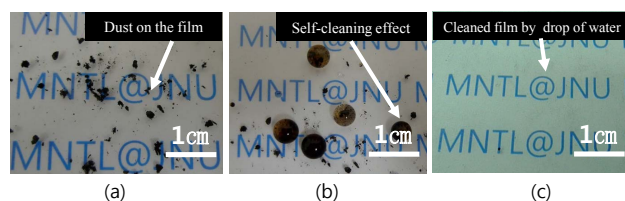
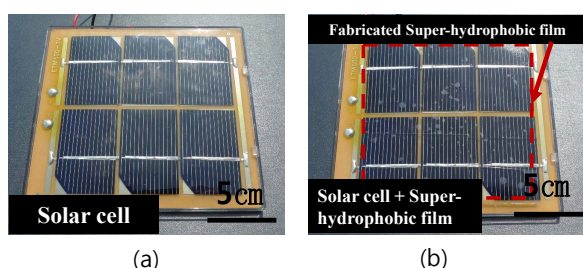


Figure 6. (a-c) Optical images showing the self-cleaning capability of ultra-hydrophobic PDMS film.



### (c) APPLICATION OF PROPOSED THIN FILM

In order to verify the utility of the self-cleaning transparent thin film, it is covered onto a solar panel as shown in Fig. 7 (a) and (b). Because solar cells use sunlight as an energy source, they are exposed to the outside environment. Accordingly, the surface of the solar cell is often contaminated by environmental dusts and amount of light transmission is reduced, thereby lowering the photoelectric conversion efficiency. In the field of solar cells, it requires an antifouling film with high transparency so that it does not affect energy efficiency while maintaining its own cleanliness without special management. The duplicated super-hydrophobic PDMS thin film is fully covered on the solar panel with a size of 15 cm × 15 cm. No chemical treatment and adhesive layer is required upon adhering, and even when they removed. The energy loss is compared with the output voltage before and after the PDMS film attachment. Four different light sources of fluorescent lamp, LED light, yellow light, and sunlight are employed for the characterization. As a result, there was about 11% voltage loss in fluorescent lamp and LED light. However, the output voltage is slightly increased under the yellow light condition. Under the sunlight condition, the solar cell has the highest output voltage, and the voltage loss is just around 1%. Such high optical transmittance is greatly beneficial to apply this super-hydrophobic PDMS to various applications.



Type of the light	Output voltage ( V )		
	Solar cell	Solar cell covered super-hydrophobic film	rate of change (%)
Fluorescent lamp	1.24	1.10	11.29
LED light	1.84	1.63	11.41
Yellow light	0.66	0.68	-3.03
Sunlight	3.47	3.43	1.15

Figure 7 Optical images of (a) solar cell, (b) solar cell covered with super-hydrophobic film.

### CONCLUSION

This paper demonstrates an effective method for the fabrication of transparent super-hydrophobic PDMS thin film. The use a reusable photo-curable polymer as a mold is also suitable for mass production. Employment of the photo-curable polymer as a reusable mold extremely simplify the production process of the unique PDMS thin films. Nano-silica coating is effective to improve the hydrophobicity of the PDMS thin film. The new fabrication process and successful experimental results reveal that the proposed idea has significant potential for diverse use of the super-hydrophobic PDMS thin film.

### ACKNOWLEDGEMENTS

This study was supported by International Collaborative R&D Program through KIAT grant funded by the MOTIE(N0000894), the "Leads Industry-university Cooperation" Project, supported by the Ministry of Education, Science & Technology (MEST) (No.2016-C-0023-010104) and the Commercialization Promotion Agency for R&D Outcomes(COMPA) funded by the Ministry of Science, ICT and Future Planning(MSIP) (No.2016K000209)

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### CONTACT

\*D.W. Lee, tel: +82-062-530-1684; mems@jnu.ac.kr