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To cite this article: Jongsung Park *et al* 2018 *Jpn. J. Appl. Phys.* **57** 06HJ09

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Polyurethane-acrylate-based hydrophobic film: Facile fabrication, characterization, and application

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Received November 30, 2017; revised January 22, 2018; accepted February 22, 2018; published online May 17, 2018

Polyurethane-acrylate (PUA) is a versatile UV-curable polymer with a short curing time at room temperature, whose surface structure can be flexibly modified by applying various micropatterns. In this paper, we propose a facile and cost-effective fabrication method for the continuous production of an optically transparent PUA-based superhydrophobic thin film. Poly(dimethylsiloxane) (PDMS) was employed as a soft mold for the fabrication of PUA films through the roll-to-roll technique. In addition, nanosilica was spray-coated onto the PUA surface to further improve the hydrophobicity. The fabricated PUA thin film showed the highest static water contact angle (WCA) of $\sim 140^\circ$. The high durability of the PUA film was also demonstrated through mechanical impacting tests. Furthermore, only $\sim 2\%$ of voltage loss was observed in the solar panel covered with the PUA-based superhydrophobic film. These obtained results indicate the feasibility of applying the film as a protective layer in applications requiring a high transparency and a self-cleaning effect. © 2018 The Japan Society of Applied Physics

1. Introduction

Water repellency or hydrophobicity is the property of a material representing difficulty of water to adhere it.¹⁾ This property is useful in the applications that require self-cleaning and contamination removal of surfaces. Therefore, various approaches have been proposed to create an artificial superhydrophobic surface.²⁻⁷⁾ One of such approaches is based on imitating natural superhydrophobic surfaces.⁸⁻¹³⁾ For example, some micro/nanoscale structures have been fabricated using materials such as silicon, poly(tetrafluoroethylene) (PTFE), and carbon nanotubes.¹⁴⁻²³⁾ However, the limitations in those previous studies were the low transparency of the fabricated super-water-repellent films and the complexity of the manufacturing methods. A high optical transmittance of the material surface is highly desired for various applications. To overcome those drawbacks, in our previous research study, we proposed a method of producing a highly optically transparent and superhydrophobic film made from poly(dimethylsiloxane) (PDMS).^{24,25)} The PDMS-based super-water-repellent film is fabricated using the conventional photolithography process. In this method, a photoresist (PR) mold is patterned under soft-baking and underexposure conditions to achieve the hierarchical micro/nanostructure. Nevertheless, another problem with this approach is that the PR mold completely dissolves in the PR stripping solution during the superhydrophobic film releasing step. Owing to this issue, this method is time-consuming when the repetition of the entire fabrication process is required. The PR mold also has a slightly different shape each time it is produced. Therefore, it cannot be applied in the scalable fabrication of highly transparent superhydrophobic films.

In this paper, we present the details of a film fabrication method that addresses the above-mentioned issues. This method consists of the application of the roll-to-roll technique and a reusable mold. First, a micropost array was prepared on a 4-in. silicon wafer using an SU-8 photosensitive polymer. The micropatterns with an optimized pitch distance were then transferred to the PDMS mold through a simple casting-curing process. Finally, the PUA-based ultra-

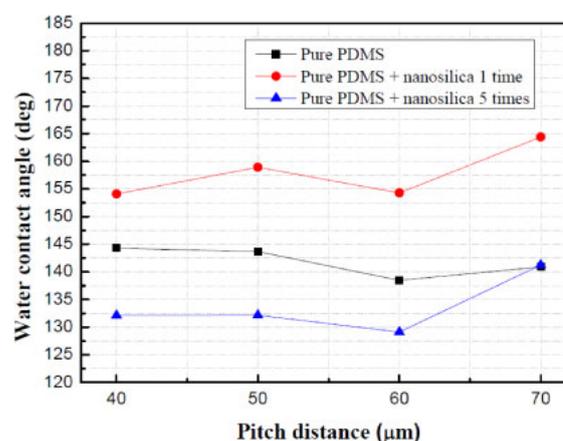


Fig. 1. (Color online) Relationship between the pitch distance and WCA of different PDMS films.

water-repellent film was produced in a large scale by the roll-to-roll technique. The different characterizations of the film in terms of hydrophobicity and durability were reported. Furthermore, the demonstrated self-cleaning and transparent characteristics was also conducted using a solar panel.

2. Experimental methods

Protective surfaces or films used in glass or solar cells require a high light transmittance and a high water repellency. Unfortunately, these two properties are competitive in the same material. For instance, the hydrophobicity of a surface will increase if its roughness increases or the pitch distance of surface structures decreases, but, its transparency will decrease. Therefore, the meticulous optimization of the surface roughness is crucial to satisfying the demands of superhydrophobicity and transparency. For this reason, different micropost-patterned PDMS films with various pitch distances were used to optimize the roughness parameters. Their corresponding water contact angles (WCAs) were measured and are shown in Fig. 1. From the figure, the WCA of the pure PDMS was observed to increase to $\sim 145^\circ$ when the pitch distance was only $40\mu\text{m}$. When the pitch distance

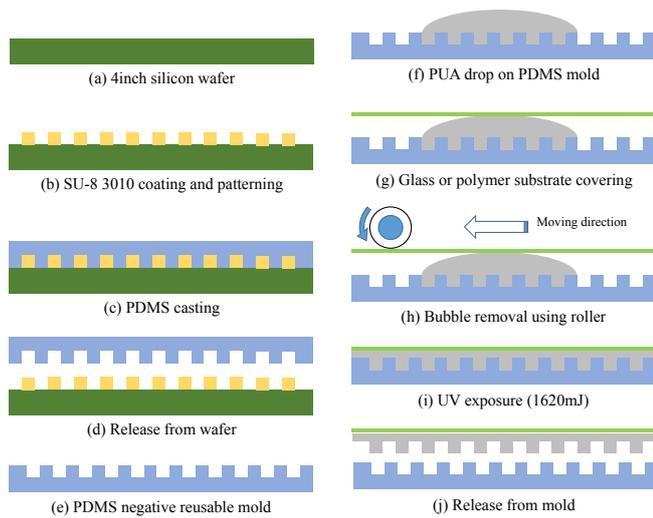


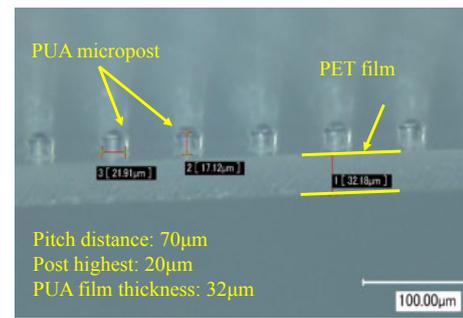
Fig. 2. (Color online) Fabrication process flow of the PUA-based superhydrophobic thin film.

was increased to $70\ \mu\text{m}$, the WCA of the pure film decreased to $\sim 140^\circ$, whereas the transparency of the film was much higher than that of the film with a pitch distance of $40\ \mu\text{m}$. Therefore, the micropost array was designed with a post diameter of $20\ \mu\text{m}$ and a pitch distance of $70\ \mu\text{m}$. Also, the PUA-based hydrophobic film showed behaviors similar to those of the PDMS-based hydrophobic film (Figs. S1 and S2 in the online supplementary data at <http://stacks.iop.org/JJAP/57/06HJ09/mmedia>).

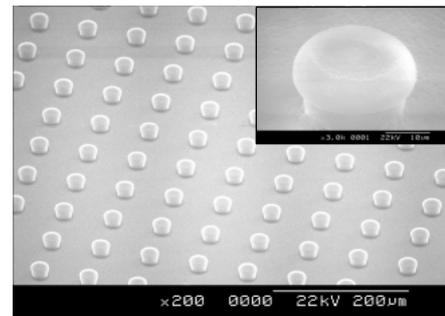
The entire process of fabricating an optically transparent PUA-based superhydrophobic thin film is shown in Fig. 2. First, an SU-8 2050 negative photoresist (MicroChem) was spin-coated on a 4-in. silicon wafer at 4,000 rpm in 30 s. Second, the wafer with an SU-8 thin layer was soft-baked at 65°C for 1 min and gradually heated to 95°C for continuous baking in 6 min. Next, it was slowly cooled to room temperature in 2 h. The soft baking step was followed by UV exposure with a dose of $140\ \text{mJ}/\text{cm}^2$. Then, postexposure baking (PEB) was performed at 65°C for 1 min and 95°C for 6 min. After PEB, a micropillar pattern was developed in an SU-8 developer solution (MicroChem) with gentle stirring and cleaned with isopropyl alcohol. Finally, the sample was dried using a nitrogen gun [Fig. 2(b)].

To fabricate the PDMS soft mold, the elastomer base (Dow Corning Sylgard 184A) and curing agent (Dow Corning Sylgard 184B) were well mixed together in a weight ratio of 10 : 1. The mixture was then degassed for 1 h to remove air bubbles created by the mixing step. Next, it was poured onto the positive SU-8 micropost-patterned wafer [Fig. 2(c)]. Subsequently, the wafer with the PDMS layer was cured at 80°C for 2 h on a hot plate. Finally, the cured PDMS film with the negative micropost array was gently peeled off from the wafer [Fig. 2(d)]. Figure 2(e) shows the cross-sectional schematic of the PDMS mold with microposts.

For the mass or continuous production of hydrophobic film, the master or PDMS mold was fixed on a flat plate in vacuum and then $\sim 100\ \mu\text{l}$ drops of UV-curable PUA resin (MINS-311RM, Changsung Sheet) were added onto the master or negative PDMS mold [Fig. 2(f)].^{26–29} A poly(ethylene terephthalate) (PET) film or glass substrate was employed as a supporting or handling layer [Fig. 2(g)].



(a)



(b)

Fig. 3. (Color online) Optical microscopy images of (a) cross section and (b) top view of the fabricated PUA film.

Subsequently, PUA was uniformly coated on the PDMS mold using a roller. The air bubbles formed inside the PUA prepolymer solution were forced out by the rolling pressure [Fig. 2(h)]. The PUA coated on the PDMS mold was then exposed to UV light with an energy of $\sim 1620\ \text{mJ}/\text{cm}^2$ [Fig. 2(i)]. Lastly, the fully cured PUA film was released from the master mold [Fig. 2(j)] and spray-coated with a commercial nanosilica solution. The flexible PDMS mold was reused to continuously fabricate the PUA-based superhydrophobic film. In addition, static water contact measurements were performed systematically in a constant temperature and humidity environment using a commercial contact angle analyzer (Surface Electro Optics Phoenix300). The durability and stability tests of the hydrophobic film were also conducted by attaching and peeling off Scotch tape (3M 810D).

3. Results and discussion

The optical microscopy images of the fabricated superhydrophobic film with a PET supporting layer are shown in Fig. 3. The PUA film had a post diameter of $20\ \mu\text{m}$ and a pitch of $70\ \mu\text{m}$. The thickness of the PET substrate was about $32\ \mu\text{m}$ and the height of the PUA posts was about $17\text{--}20\ \mu\text{m}$ [see Fig. 3(a)]. Figure 3(b) confirms the uniformity of the micropost patterns across the fabricated PUA film when all the posts had an identical circular cylinder shape. The micropost with a cylindrical structure was slightly changed to that with a mushroom-shaped structure after coating the nanosilica [inset of Fig. 3(b)]. The superhydrophobicity of the fabricated film was experimentally determined by measuring its static WCA. In particular, the nanosilica-coated superhydrophobic film had a higher static WCA of about 140° than the noncoated film, as shown in Fig. 4(a). In

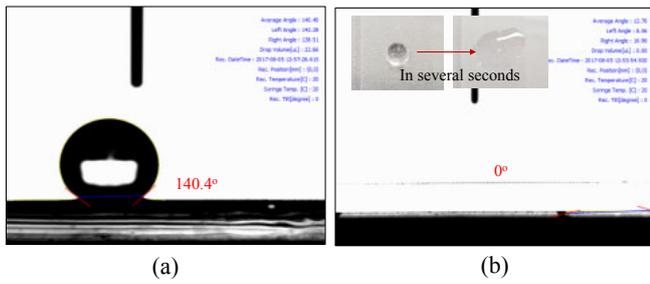


Fig. 4. (Color online) Water contact angles of (a) nanosilica-coated and (b) pristine PUA films.

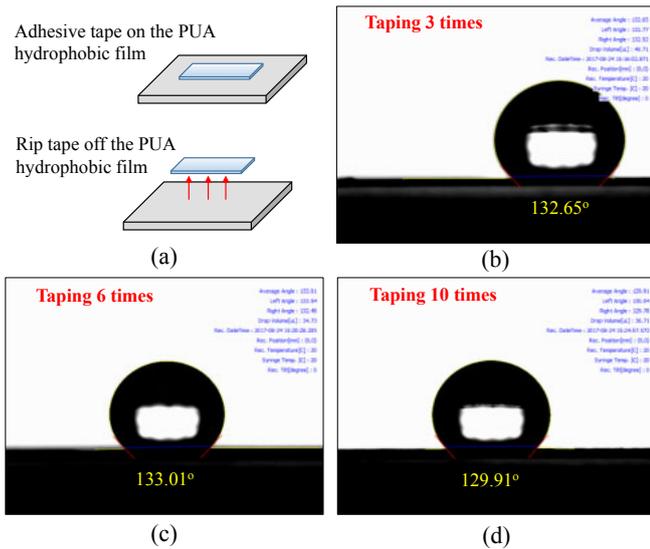


Fig. 5. (Color online) (a) Schematic of experimental setup for mechanical reliability test. Optical images of water droplet on patterned PUA film after taping (b) 3, (c) 6, and (d) 10 times.

general, PUA is hydrophilic with a static WCA of $\sim 60^\circ$.³⁰⁾ The WCA can be increased to 115° by coating nanosilica on to the PUA surface. Unlike in the case of spray coating nanosilica, the micro-PUA structures formed on the surface increased the WCA of the film of the material, but this phenomenon lasted only a few seconds owing to the hydrophilic nature of the material [Fig. 4(b)]. The reason for this is that the nanosilica coated on to the PUA surface helps to confer a continuous water repellency by lowering the surface energy of the film.

To evaluate the stability of the superhydrophobicity of the film, the tape test was carried out by attaching and detaching Scotch tape from the nanosilica-coated PUA film. Figure 5(a) shows a schematic of the experimental method used to verify the long-term reliability of the superhydrophobic thin film. Before conducting the test, the static WCA of the film was $\sim 140^\circ$. On the other hand, the average static WCAs of the film after 3, 6, and 10 repetitions of tape attaching-detaching cycles were 132, 133, and 129° , respectively [Figs. 5(b)–5(d)]. These results clearly proved that the superhydrophobicity of the nanosilica-coated PUA film is stable despite the repeated tape attaching-detaching cycles. The advantage of patterning the PUA surface with a micropost array is more clearly demonstrated in Fig. 6. Initially, the flat nanosilica-coated PUA film had a WCA of $\sim 115^\circ$. Nevertheless, the WCA of the film dropped to ~ 76 and 33° after only 1 and 2

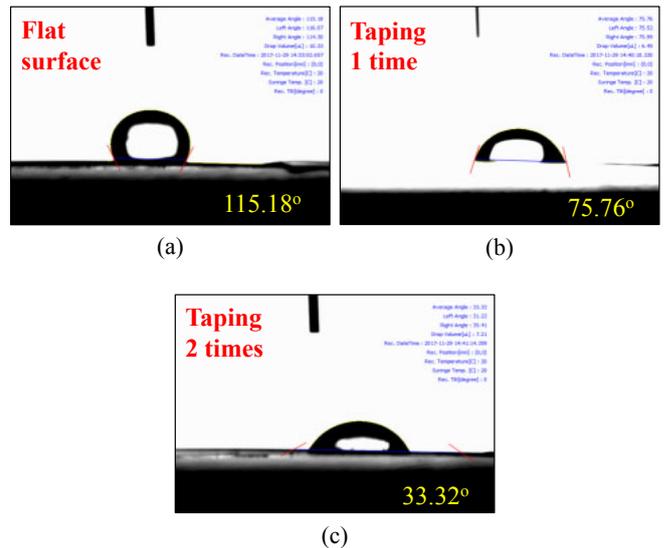


Fig. 6. (Color online) Optical images of water droplet on flat PUA film (a) before and after taping (b) 1 and (c) 2 times.

Table I. Measured WCAs taping test of PUA film (unit: deg).

	Nanosilica coat	Taping time				
		1	2	3	6	10
PUA without micropost	115.18	75.76	33.32	0 ^{a)}	0 ^{a)}	0 ^{a)}
PUA with micropost	140.40	135.30	134.84	132.65	133.01	129.91

a) Fully wetted.

times of 3M Scotch tape contact (Table I). The reason for this is that, without any micro structures on the surface, the PUA film cannot retain the coated nanosilica. In the case of microstructures on the PUA surface, the nanosilica coated on the sidewalls between the posts is maintained even though the nanosilica on the top of the posts is removed by external force. Furthermore, it was confirmed that there was almost no change in transparency with or without nanosilica coating (see Fig. S3 in the online supplementary data at <http://stacks.iop.org/JJAP/57/06HJ09/mmedia>).

Figures 7(a) and 7(b) show the optical images of the water-repellent PUA film fabricated on a glass substrate and added with drops of water. In addition, Fig. 7(c) displays the image of the PUA film fabricated on a PET film. These images prove the flexibility of the roll-to-roll technique since it can be applied to different supporting layers. The transparency of the PUA-PET film was experimentally confirmed by using paper with black print on a white background, as shown in Fig. 7(d). A superior self-cleaning effect was also confirmed experimentally.

To further verify the light transmittance of the fabricated PUA-PET superhydrophobic film, solar panels with and without the film were compared (Fig. 8). Then, we examined whether the optically transparent superhydrophobic thin film adhered to the solar surface degrades the the power generation efficiency of the solar panel. The output voltages of the solar panels with and without PUA-PET superhydrophobic film were measured using different light

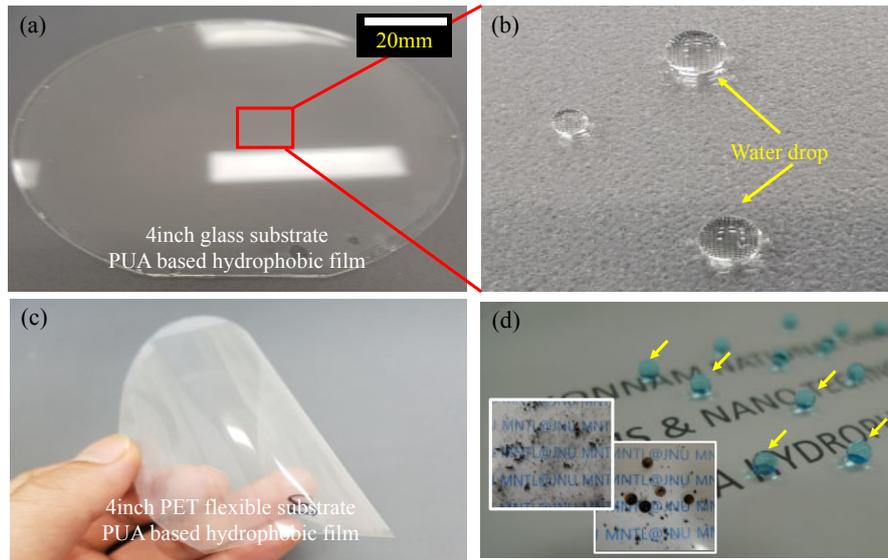


Fig. 7. (Color online) Fabricated PUA-based superhydrophobic film. (a) Glass-based PUA hydrophobic film. (b) Water drop on glass-based PUA hydrophobic film. (c) PET hydrophobic film flexibility test. (d) PET-based flexible superhydrophobic film and water drop.

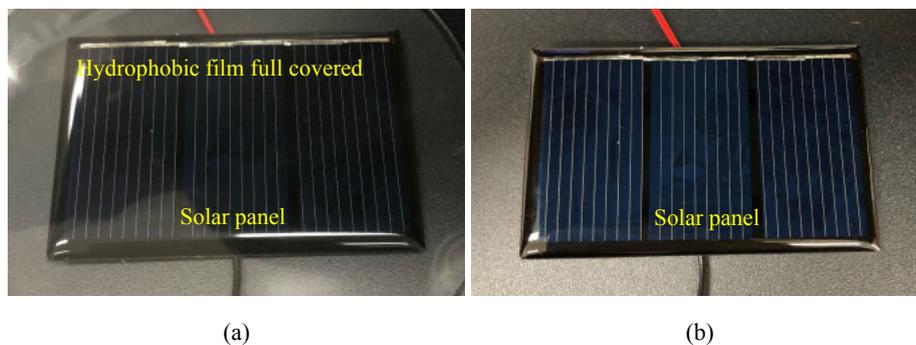


Fig. 8. (Color online) Optical images of solar panels (a) with and (b) without the fabricated superhydrophobic film.

Table II. Output voltage of solar panels with and without PUA superhydrophobic film attachment (unit: V).

	With PUA hydrophobic film	Solar panel only
Solar light	1.25	1.27
LED (white)	0.74	0.77
LED (yellow)	0.66	0.69

sources, as indicated in Table II. In particular, ~4% voltage loss was observed in the attached solar panels exposed to white and yellow LED light sources. Moreover, the sunlight test showed only a ~2% voltage drop. These results suggest that solar panels can be protected from contamination without affecting their power generation efficiency, owing to the high transparency of the produced superhydrophobic film.

4. Conclusions

An effective method of fabricating a PUA-based superhydrophobic film was reported. The proposed roll-to-roll technique employing a reusable PDMS mold showed great promise for the mass production of PUA ultra-water-repellent film. Furthermore, the noteworthy features of the fabricated film are a high optical transmittance and superhydrophobicity with the highest water contact angle of 140°. The durability

and transparency of the fabricated PUA film were also demonstrated through various practical methods. In the future, it is highly possible to extend the usefulness of the proposed method in the mass production of optically transparent superhydrophobic films.

Acknowledgments

This research was supported by 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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