Research Article

Micro/nano-suction cup structure of silicone rubber fabricated by ArF excimer laser

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Abstract
Micro/nano-suction cups of silicone rubber, cylindrical swelling structures in micron size with a hole of hundreds nanometer diameter each, were fabricated by 193-nm ArF excimer laser-induced photodissociation of silicone rubber. To be periodically, silica glass microspheres of 2.5 μm diameter were aligned on silicone rubber via Al thin film during laser irradiation. The Al thin film underneath each microsphere was locally laser-ablated to enable a circular irradiation of subsequent laser pulses, then the exposed silicone rubber was photochemically swelled by the photodissociation of Si–O bonds of silicone rubber. Also, debris of aluminum surrounding the laser-ablated areas resulted in pushing microsphere up to adjust a focal point to the surface of silicone rubber to form a hole centered at each the swelled silicone. The fabricated structure showed clear superhydrophobic properties. Dependence of single pulse fluence of ArF excimer laser on the fabrication of micro/nano-suction cup structure was discussed, together with the variation of thickness of Al thin film from 10 to 100 nm. The use of the superhydrophobic silicone rubber we fabricated is expected as a kind of delivery system, toward holding a small object even in water by each micro/nano-suction cup structure.

Keywords Micro/nano-suction cup · Silicone rubber · ArF excimer laser · Al thin film · Superhydrophobic property

1 Introduction

Vacuum-UV (VUV) pulsed lasers commercially available, ArF excimer laser (193 nm) and F_2 laser (157 nm), are capable of inducing strong photochemical reactions on material surface [1, 2]. For instance, a polytetrafluoroethylene (Teflon) which is a chemically stable polymer was successfully modified into high oleophilic or hydrophilic properties by the irradiation of ArF excimer laser [1, 3–5]. As a result, the photochemically modified polytetrafluoroethylene showed high adhesion strength with an epoxy adhesives [6]. The F_2 laser also enables a unique photochemical surface modification of a polydimethylsiloxane (silicone) rubber into a pure silica glass (SiO_2) [2, 7, 8]. Based on the modification, a SiO_2 optical waveguide or SiO_2 microlens array has been successfully fabricated on a flexible substrate of silicone rubber [9–12]. Also, this modification has been applied to surface hardening of silicone for developing a lightweight automobile window [13–15]. Such the VUV pulsed lasers are employed for not only the photochemical surface modifications but also materials processing by laser ablation [16–18]. In any cases, the high photon energies and thin penetration depths of material at these wavelengths are important for achieving the unique materials processing.

Recently, when the ArF excimer laser irradiated a silicone rubber, instead of F_2 laser, the photochemical swelling phenomenon which is due to the photodissociation of Si–O bonds of silicone rubber was found on the surface [19, 20]. Microspheres made of SiO_2 in micron size were used for fabricating the periodic microswelling structure of silicone rubber, resulting in high superhydrophobic properties [21, 22]. A hydrophobic or superhydrophobic silicone is useful for industrial and biomedical applications

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[23, 24]. As useful references, the fabrications of regular patterns on polycarbonate by ArF excimer laser are also available [25, 26]. In the series of our work, very recently, a frusto-conical shape of the obtained microswelling structure could be changed to cylindrical by just depositing an Al thin film between microspheres and silicone rubber during laser irradiation, for the use as a micro/nano-suction cup [27, 28]. The novelty of this work is that the successful fabrication of micro/nano-suction cup structure of silicone rubber through the ArF excimer laser-induced photochemical reactions. The structure is difficult to be realized by conventional molding process.

In this paper, to find a processing window for the fabrication of the periodic micro/nano-suction cup structure, we extend the recent experiment to the dependence of single pulse fluence of ArF excimer laser on the fabrication of the structure, together with the variation of thickness of Al thin film. An optimum condition of laser irradiation and thickness of Al thin film was derived from the present experiment, in addition to the reference to our previous work as complement data [28]. Measurement of contact angle of water was continuously carried out for realizing the superhydrophobic properties, still toward holding a small object in water as a kind of delivery system [27].

2 Experimental procedure

Schematic illustration of the experimental procedure is shown in Fig. 1. For the fabrication of micro/nano-suction cup structure of silicone rubber, silica glass microspheres of 2.5 µm diameter (Nippon Shokubai KE-P250) were aligned on Al-deposited, 2-mm-thick silicone rubber before laser irradiation. The experimental procedure has been described in our previous work [27, 28]. To revisit the basic concept, an Al thin film was firstly deposited on the silicone rubber by a vacuum evaporation of Al wire. The thickness of Al thin film was varied from approximately 10 to 50 and 100 nm, which were measured beforehand on a slide glass using a stylus profilometer (Veeco, Dektak[3]). Then, the microspheres were dispersed in ethanol, and the dispersed solution was dripped on the Al-deposited silicone rubber. Thus, single layer of silica glass microspheres was formed on the Al-deposited silicone rubber after the heated-air drying at 50 °C for 3 min, together with the removal of excess microspheres.

The sample was placed 80 mm apart from the outlet of the ArF excimer laser (Coherent, COMPexPro110). The beam path was filled with nitrogen gas at the flow rate of 10 L/min to avoid optical absorption of oxygen molecules

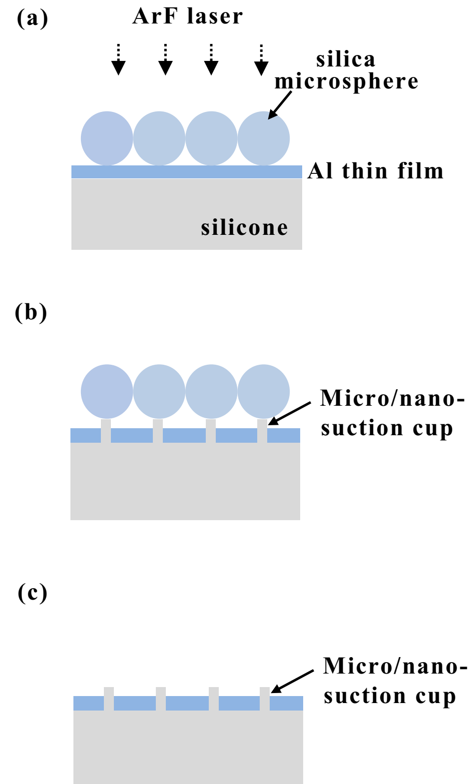

Fig. 1 Schematic illustration of the experimental procedure; **a** ArF excimer laser irradiation, **b** swelling of the laser-irradiated area, and **c** removal of silica glass microspheres

in air. A 10 × 10 mm^2 aperture was set on the outlet of the ArF excimer laser to use a homogeneous beam profile. The ArF excimer laser irradiated the sample surface without any optics. Thus, laser pulse energy was equal to the single pulse fluence. The single pulse fluence of the ArF excimer laser was changed from approximately 2 to 5, 10, 20 and 30 mJ/cm^2. The pulse repetition rate was kept constant at 1 Hz. The pulse duration was approximately 20 ns. The laser pulse number was changed from 15 to 60, 900 and 1800. After the laser irradiation, silica glass microspheres were removed by a 1 wt% HF chemical etching for 90 s and subsequent ultrasonic washing in ethanol for 10 min. Occasionally, remained Al thin film among the micro/nano-suction cup structure was chemically etched by a 0.5% KOH aqueous solution for 30 min.

Morphology of the sample surface was observed by a scanning electron microscope (SEM, Phenomworld, Pro). Shape of the swelling structure fabricated by laser irradiation was imaged by an atomic force microscope (AFM, Hitachi, AFM5100N). To see superhydrophobic properties of the samples, a static contact angle of water was measured.

3 Results and discussion

Figure 2 shows the SEM images of the silicone rubber surfaces after ArF excimer laser irradiation and after removal of silica glass microsphere. The laser pulse number was kept at 15. The thickness of Al thin film was approximately 10 nm. To observe the laser-irradiated areas underneath each microsphere clearly, a subsequent chemical etching of the Al thin film was carried out by immersing the samples in the KOH aqueous solution for 30 min. In the case of 2 mJ/cm^2 (Fig. 2a), the laser-irradiated areas in white were recognized. When the laser fluence increased to 5 mJ/cm^2 (Fig. 2b), circular areas of approximately 680 nm diameter in white were seen, together with circles of approximately 270 nm diameter in black. At 10 mJ/cm^2 (Fig. 2c), the circular areas in white was slightly expanded to be approximately 720 nm diameter, together with circles of approximately 270 nm diameter in black.

To see the structure of the laser-irradiated areas of silicone rubber, the samples shown in Fig. 2 were imaged by the AFM, as shown in Fig. 3. In the case of 2 mJ/cm^2 (Fig. 3a), the laser-irradiated areas slightly swelled. When the laser fluence increased to 5 mJ/cm^2 (Fig. 3b), the laser-irradiated areas clearly swelled. A hole centered at each the swelled silicone rubber was also observed, which is corresponding to the circle in black shown in Fig. 2b. A large difference between the samples at 5 and 10 mJ/cm^2 was not seen in the swelled structure (Fig. 3c). On the other hand, the laser-irradiated areas were ablated at the fluence of approximately 20 mJ/cm^2 and over, as mentioned below.

Figure 4 shows the SEM images of the silicone rubber surfaces after ArF excimer laser irradiation and after removal of silica glass microsphere. In this case, the laser pulse number increased to 60. The thickness of Al thin film was kept at approximately 10 nm. After the subsequent KOH chemical etching, in the case of 2 mJ/cm^2 (Fig. 4a), circular areas of approximately 670 nm diameter in white were seen, together with circles of approximately 220 nm diameter in black. When the laser fluence increased to 5 mJ/cm^2 (Fig. 4b), circular areas of approximately 720 nm diameter in white were seen, together with circles of approximately 270 nm diameter in black. At 10 mJ/cm^2 (Fig. 4c), the circular areas in white was slightly expanded to be approximately 800 nm diameter, together with circles of approximately 350 nm diameter in black.

Figure 5 shows the AFM images of the samples shown in Fig. 4. In the case of 2 mJ/cm^2 (Fig. 5a), the laser-irradiated areas clearly swelled. A hole centered at each the swelled silicone rubber was also confirmed.

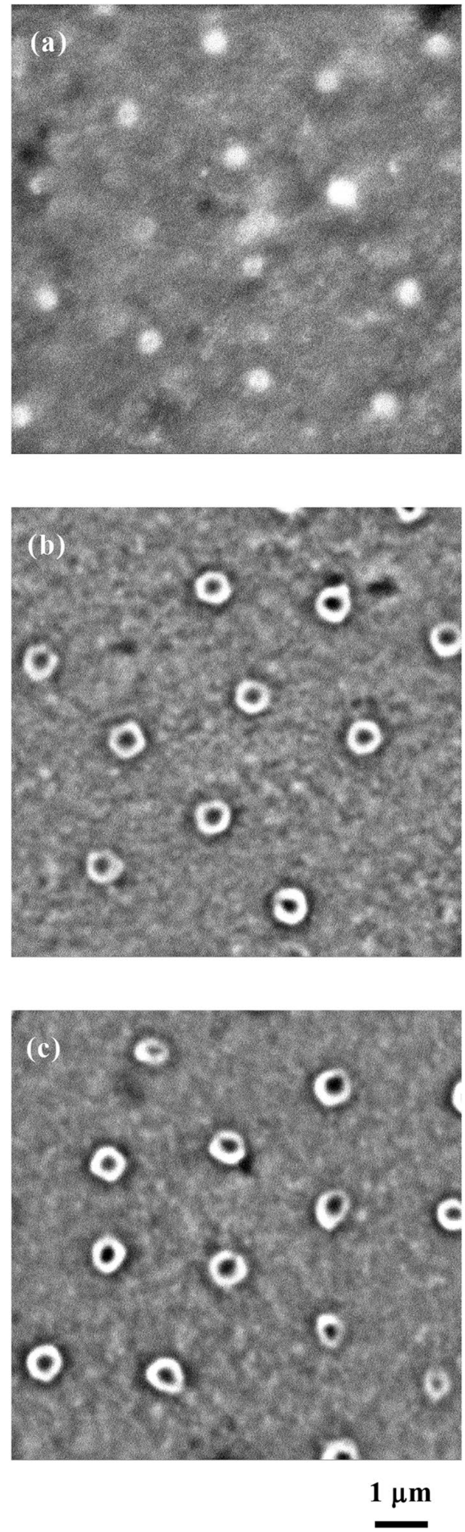

Fig. 2 SEM images of the silicone rubber surfaces after ArF excimer laser irradiation and after removal of silica glass microsphere, in addition to the subsequent KOH chemical etching. Thickness of Al thin film was 10 nm. Laser pulse number was 15. Laser fluence was varied from **a** 2 to **b** 5 and **c** 10 mJ/cm^2

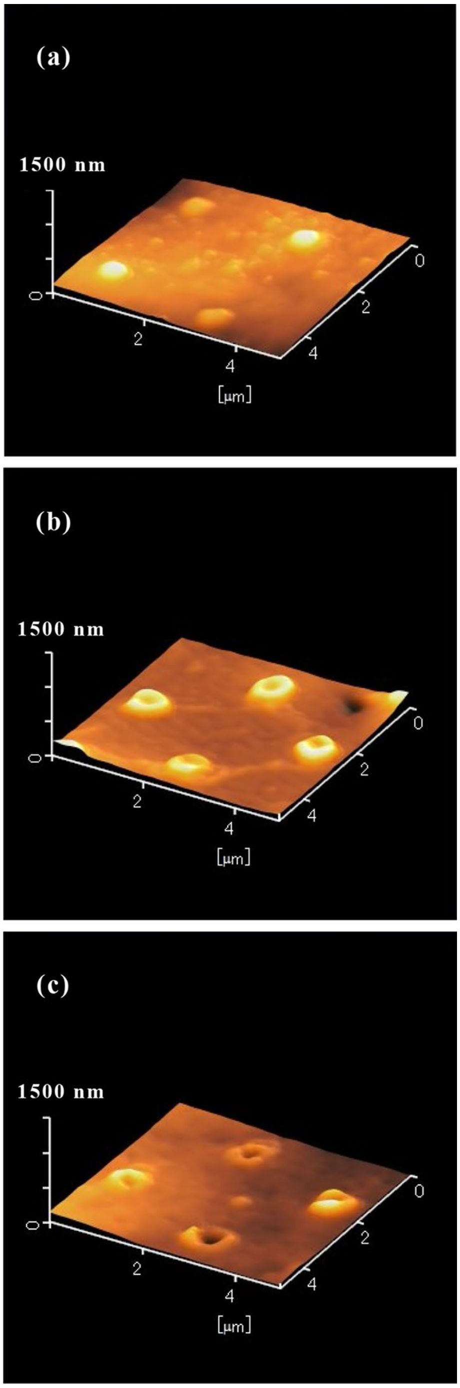

Fig. 3 AFM images of the silicone rubber surfaces after ArF excimer laser irradiation and after removal of silica glass microsphere, in addition to the subsequent KOH chemical etching. Thickness of Al thin film was 10 nm. Laser pulse number was 15. Laser fluence was varied from **a** 2 to **b** 5 and **c** 10 mJ/cm^2

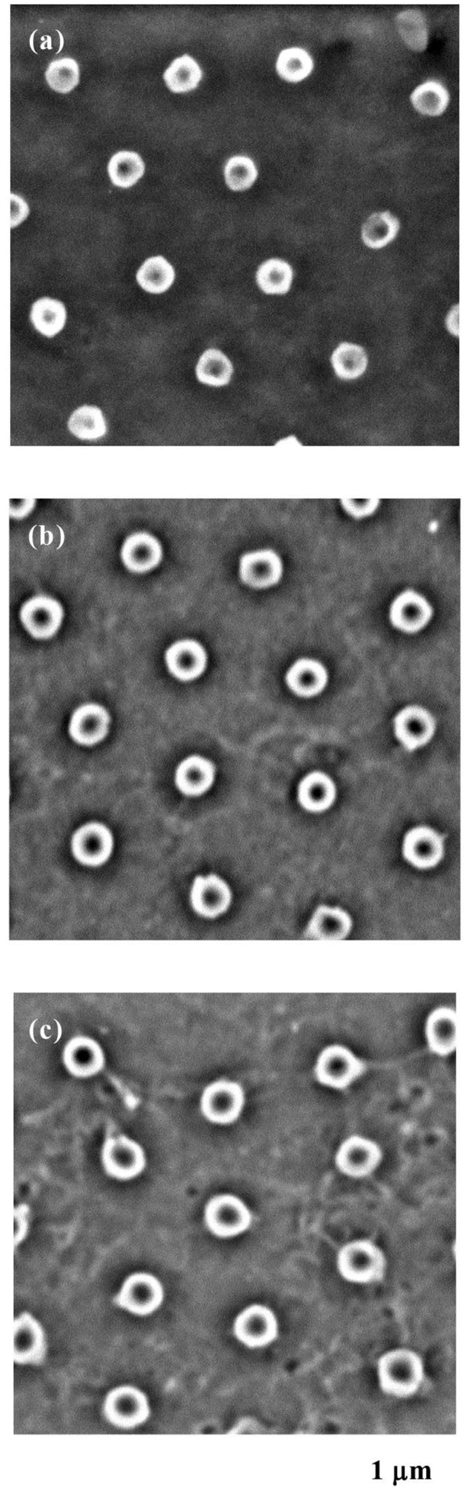

Fig. 4 SEM images of the silicone rubber surfaces after ArF excimer laser irradiation and after removal of silica glass microsphere, in addition to the subsequent KOH chemical etching. Thickness of Al thin film was 10 nm. Laser pulse number was 60. Laser fluence was varied from **a** 2 to **b** 5 and **c** 10 mJ/cm^2

When the laser fluence increased to 5 mJ/cm^2 (Fig. 5b), the laser-irradiated areas clearly swelled and the height increased. At 10 mJ/cm^2 (Fig. 5c), a hole diameter also increased clearly. Thus, the single pulse fluence of ArF

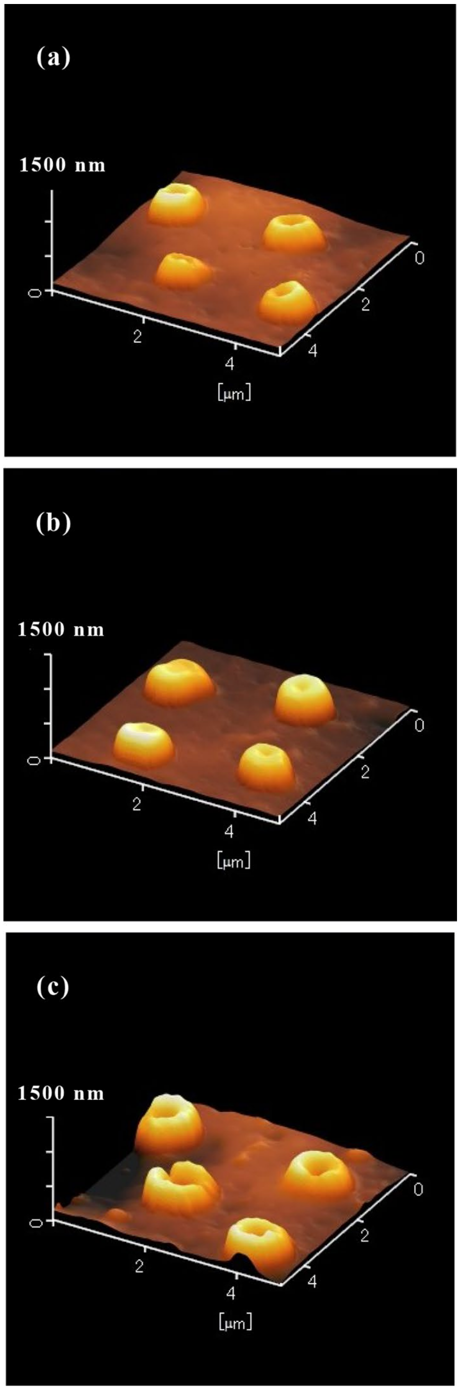

Fig. 5 AFM images of the silicone rubber surfaces after ArF excimer laser irradiation and after removal of silica glass microsphere, in addition to the subsequent KOH chemical etching. Thickness of Al thin film was 10 nm. Laser pulse number was 60. Laser fluence was varied from **a** 2 to **b** 5 and **c** 10 mJ/cm^2

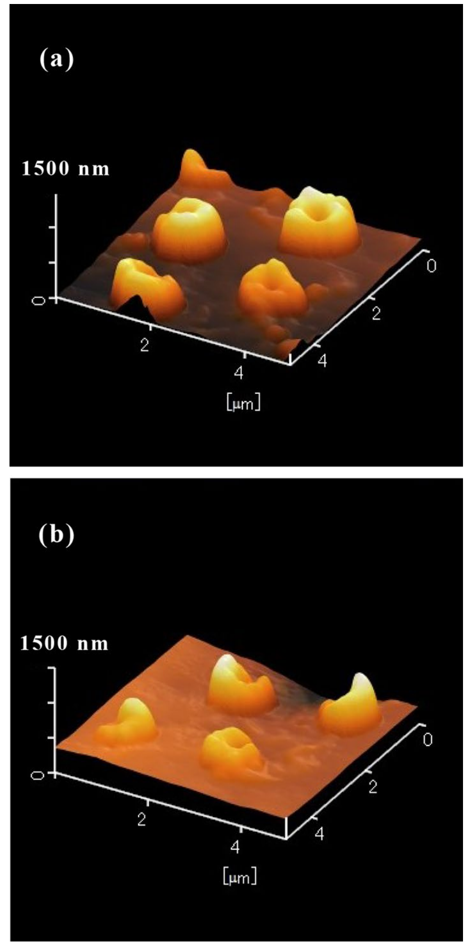

Fig. 6 AFM images of the silicone rubber surfaces after ArF excimer laser irradiation and after removal of silica glass microsphere, in addition to the subsequent KOH chemical etching. Laser fluence was 10 mJ/cm^2. Laser pulse number was 60. Thickness of Al thin film was **a** 50 and **b** 100 nm

excimer laser is capable of changing the diameter of the swelled structure. In addition, as the formation of the holes is based on laser ablation, the hole diameter would be changeable by varying the laser fluence. However, the depth of the holes in the swelling silicone cannot be measured accurately even by the AFM at this point. At the early stage of the swelling below 60 laser pulses, the diameters of swelling and hole and the height of swelling were not able to be controlled independently by changing the single pulse fluence or pulse number of ArF excimer laser.

Compared to the case in Fig. 5c, the thickness of Al thin film increased from 10 to 50 and 100 nm, as shown in Fig. 6. Again, the laser fluence and laser pulse number were 10 mJ/cm^2 and 60, respectively. Judging from Fig. 6a, b, the shape of each the swelled structure became uneven by increasing the thickness of Al thin film. In our previous work, when an Al thin film was deposited on silicone rubber, the surface morphology showed a textured structure [21, 22]. The average roughness increased with increasing the thickness of Al thin film to be roughly 40–50 nm [22], meanwhile the roughness of 50 and 100-nm Al thin films was approximately 0.6–1.5 nm on a slide glass. Thus, the ablation of Al thin film caused by focusing the laser with each microsphere occurs irregularly because each the focal point becomes irregular due to the textured structure of Al thin film. In addition, when the Al thin film becomes thicker, more number of photons might be required for making the through hole of Al thin film.

Though the role of the Al thin film for forming a hole centered at each swelled silicone rubber was previously discussed [28], the understandings are briefly revisited. Qualitatively, a focal point of ArF excimer laser could be shifted to the surface side by depositing the textured Al thin film, resulting in exceeding a laser ablation threshold of silicone rubber at 193 nm wavelength. Moreover, debris of the ablated Al thin film might also push up the microsphere to move the focal point closer to the surface. Also, the change of focal point due to shockwave caused by laser ablation might be considered. As another possibility, to form the center hole, the localized ArF excimer laser heating without material removing might occur.

Figure 7 shows the SEM image of the silicone rubber surface after ArF excimer laser irradiation and after removal of silica glass microsphere. The laser fluence and laser pulse number was 10 mJ/cm^2 and 900, respectively. The thickness of Al thin film was kept at approximately 10 nm. A cylindrical structure roughly 1 μm diameter and 2 μm height was clearly observed at the regular intervals of approximately 2.5 μm.

In order to observe the swelling structures at the laser fluences of over 10 mJ/cm^2, the fluence was varied to 20 and 30 mJ/cm^2. Figures 8 and 9 show the SEM images of the silicone rubber surfaces after ArF excimer laser and

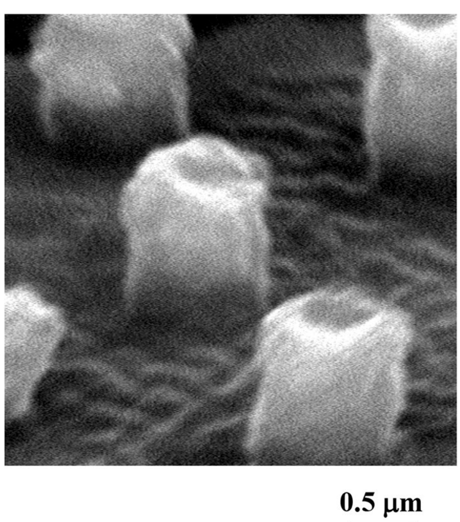

Fig. 7 SEM image of the periodic micro-suction cup structure fabricated on silicone rubber. Laser fluence was 10 mJ/cm^2. Laser pulse number was 900. Thickness of Al thin film was 10 nm

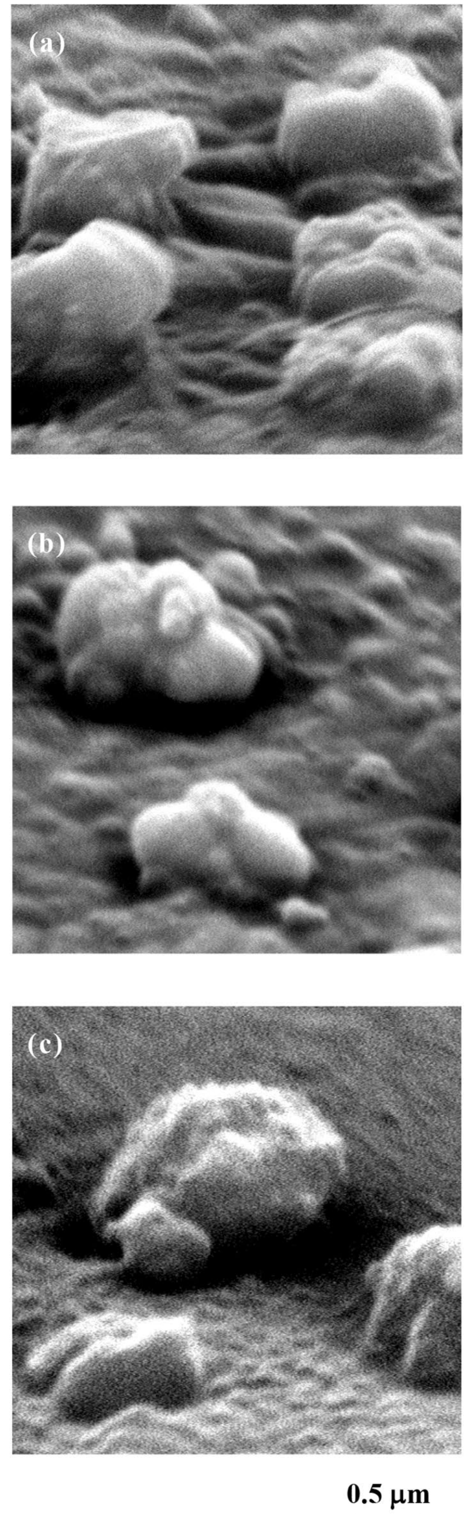

Fig. 8 SEM images of the silicone rubber surfaces after ArF excimer laser irradiation and after removal of silica glass microsphere. Laser fluence was 20 mJ/cm^2. Thickness of Al thin film was varied from **a** 10 to **b** 50, and **c** 100 nm

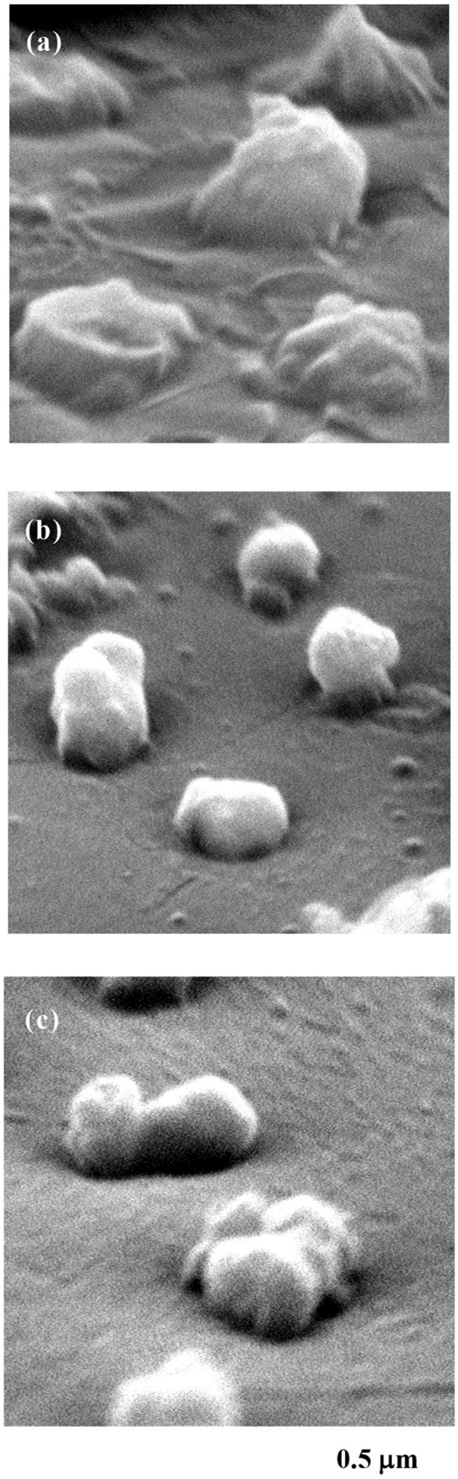

Fig. 9 SEM images of the silicone rubber surfaces after ArF excimer laser irradiation and after removal of silica glass microsphere. Laser fluence was 30 mJ/cm^2. Thickness of Al thin film was varied from **a** 10 to **b** 50, and **c** 100 nm

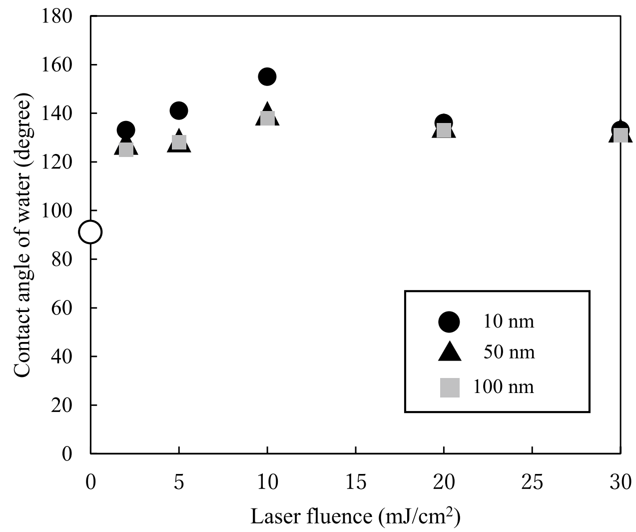

Fig. 10 Relation between the single pulse laser fluence and contact angle of water in three different thicknesses of Al thin film. Laser pulse number was 1800 in all cases

after removal of microspheres. The laser pulse number was 1800. In both cases, the swelled structures were damaged by the intense laser pulses, though the swelling was still seen. On the other hand, in our previous work [22], the cylindrical swelling structure of silicone rubber with a hole was successfully fabricated at 10 mJ/cm^2 fluence and at 1800 pulses, though the structure became uneven when the thickness of Al thin film was 50 and 100 nm. Therefore, the optimum laser fluence was approximately 10 mJ/cm^2 for fabricating the micro/nano-suction cup structure under the condition of the 10-nm Al thin film. Otherwise, at less than 10 mJ/cm^2, a long irradiation of ArF excimer laser could be acceptable.

Figure 10 shows the dependence of laser fluence on the contact angle of water at three different thicknesses of Al thin film, in order to evaluate the hydrophobic or superhydrophobic properties of the samples. The laser pulse number was 1800. Measurement of contact angle of water was described in our previous work [21, 22]. In the case of a bare silicone rubber, the contact angle was approximately 90°. To make sure, in Ref. [19], whole surface of the periodically swelled silicones of frusto-conical shape were coated with Al thin film. On the other hand, in the present experiment, the fabricated cylindrical swelling silicones were directly contacted with a water drop when measuring the contact angle. However, the textured Al thin films were remained among the swelled silicones because the KOH chemical etching was not carried out. After ArF excimer laser irradiation, over 120° of contact angle were obtained, which means that the fabrication of micro/nano-suction cup structures are easy to realize the hydrophobic properties. However, the processing window to obtain the superhydrophobic properties is narrow in the laser fluence region. To obtain the highest contact angle of water, the laser fluence of approximately 10 mJ/cm^2 was the best at each the thickness. Especially, under the condition of 10-nm Al thin film, the superhydrophobic properties, 150° and over, were successfully realized. This means that the 2 µm height, regular micro/nano-suction cup structures are required for achieving the superhydrophobic properties. The use of the superhydrophobic silicone rubber we fabricated is expected as a kind of delivery system, toward holding a small object even in water by each micro/nano-suction cup structure, for fabricating a silicone-based microdevice moving in water for electronic and biomedical applications [27].

4 Conclusions

The cylindrical swelling structures of silicone rubber in micron size with a hole of hundreds nanometer diameter each, the micro/nano-suction cup structures, were periodically fabricated by the 193-nm ArF excimer laser. The silica glass microspheres of 2.5 µm diameter were aligned on the Al-deposited silicone rubber during the laser irradiation. The Al thin film underneath each microsphere was locally laser-ablated to enable the circular irradiation of subsequent laser pulses, then the exposed silicone rubber was photochemically swelled due to the photodissociation of Si–O bonds of silicone rubber. Also, the debris of Al thin film surrounding the laser-ablated areas might push the microspheres up to adjust the focal point to the surface of silicone rubber to form a hole centered at each the swelled silicone rubber. The dependence of the single pulse fluence of ArF excimer laser was examined, together with the variation of thickness of Al thin film from 10 to 100 nm. The single pulse fluence of ArF excimer laser was capable of changing the diameter of the swelled structure. In addition, the hole diameter would be changeable by varying the laser fluence. At the early stage of the swelling below 60 laser pulses, the diameters of swelling and hole and the height of swelling were not able to be controlled independently by changing the single pulse fluence or pulse number of ArF excimer laser. The optimum single pulse fluence of ArF excimer laser was approximately 10 mJ/cm^2 for fabricating the micro/nano-suction cup structures under the condition of the 10-nm Al thin film. Otherwise, at less than 10 mJ/cm^2, a long irradiation of ArF excimer laser could be acceptable. The fabricated micro/nano-suction cup structures showed the clear superhydrophobic properties. The use of the superhydrophobic silicone rubber we fabricated is expected as a kind of delivery system, toward holding a small object even in water by each micro/nano-suction cup structure, for fabricating a silicone-based microdevice moving in water for electronic and biomedical applications.

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Compliance with ethical standard

Conflict of interest The author declare that they have no competing interests.

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