



Article

# Photochemical Micro-/Nano-Swelling of Silicone Rubber Induced by Long Pulse-Repetition Interval of an ArF Excimer Laser

Masayuki Okoshi

Department of Electrical and Electronic Engineering, National Defense Academy,  
Yokosuka 239-8686, Kanagawa, Japan; okoshi@nda.ac.jp

**Abstract:** Long pulse-repetition intervals of 100 to 500 ms of a 193 nm ArF excimer laser successfully increased the height of the photochemical micro-/nano-swelling of silicone rubber, observed with a scanning electron microscope. The effect of the interval was seen despite the heating of the silicone rubber to 80 °C during laser irradiation. The height of the micro-/nano-swelling was saturated when the laser pulse number was 300 or greater, although each of the saturated heights of the micro-/nano-swelling formed by several pulse-repetition intervals was different. Thus, a second ArF excimer laser irradiated the growing micro-/nano-swelling before the saturation; the saturated height of the growing micro-/nano-swelling could be controlled by the pulse-repetition interval of the second ArF excimer laser. To examine the process of micro-/nano-swelling, an early stage of the growth was observed using an atomic force microscope; a dent structure of the micro-/nano-swelling was clearly recognized. In addition, a needle-like structure of the micro-/nano-swelling could be formed when silica glass microspheres were sparsely aligned.

**Keywords:** micro-/nano-swelling; silicone rubber; ArF excimer laser; pulse-repetition interval; photodissociation



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## 1. Introduction

In material processing using a laser, the pulse width of the laser is one of the important parameters for exploring unique phenomena and processing. In particular, shortening the pulse width to the femtosecond (fs) scale has received attention in the micro-/nanofabrication of materials [1]. No heat-affected zone surrounding the laser-ablated area can be formed to realize precise processing of materials [2,3]. Moreover, internal processing of materials has been demonstrated through the multiphoton absorption induced by an intense fs-laser [4–6]. The fs-laser has also been applied to creating thin films and micro-crystals [7,8]. Furthermore, the pulse-repetition interval, which is the time between laser pulses, should also be considered for material processing. A double laser pulse method for annealing and laser-induced breakdown spectroscopy and the burst mode of an fs-laser for micro-/nanofabrication have been reported [9–12]. A short pulse-repetition interval of the laser is required in these cases because a second laser pulse should irradiate the transient melting/decomposing material induced by the first laser pulse. On the contrary, however, a long pulse-repetition interval of a laser of sub-second scale has not been investigated for material processing.

In our previous work, a remarkable effect of a long pulse-repetition interval of a 193 nm ArF excimer laser on the formation of the photochemical micro-/nano-swelling of silicone ( $[\text{SiO}(\text{CH}_3)_2]_n$ ) rubber was shown [13]. When the ArF excimer laser irradiates the surface of silicone rubber, the main chain of Si–O bonds of the silicone rubber is photodissociated into the lower molecules, resulting in photochemical micro-/nano-swelling in the laser-irradiated area [13–20]. Periodically, silica glass microspheres with a diameter of 2.5  $\mu\text{m}$  were aligned on the entire surface of silicone rubber during laser irradiation [21].

A long pulse-repetition interval of the ArF excimer laser successfully suppressed the photodissociation of the side-chain of CH<sub>3</sub> bonds, maintaining the chemical bonding state of silicone [13]. Thus, the height of the photochemical micro-/nano-swelling can be significantly increased. The use of an ArF excimer laser is essential for the photochemical micro-/nano-swelling in the commercially available pulsed UV lasers. Using a 157 nm F<sub>2</sub> laser, silicone rubber was photochemically modified into pure SiO<sub>2</sub> [22]. By comparison, the fourth harmonics of a Nd:YAG laser (266 nm) produced isolated carbon on silicone rubber [23]. In general, silicone rubber has excellent properties, such as resistance to heat, cold, and chemicals, high optical transparency, and high electrical insulation. By periodically applying photochemical micro-/nano-swelling, therefore, a superhydrophobic property can also be obtained on the silicone rubber, which enables the widespread application of silicone in scientific and industrial fields; for instance, our previous results led to the fabrication of a silicone rubber-based microdevice operating in the water, and a biochip under deep-UV light for disinfection [14,16,24].

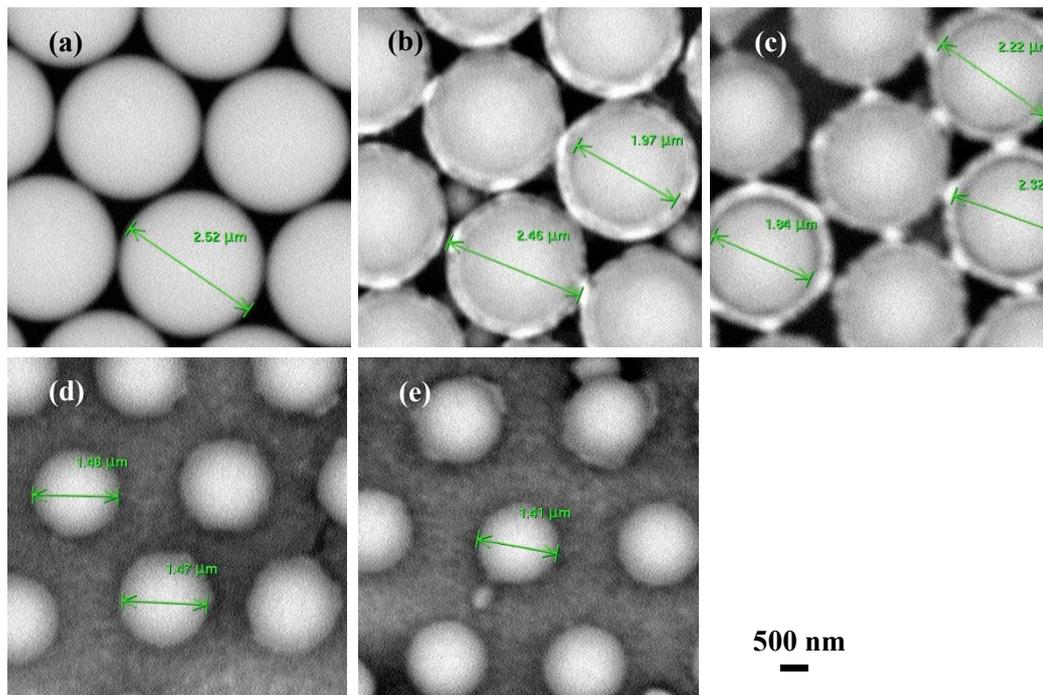
In this study, to understand the effect of the long pulse-repetition interval of an ArF excimer laser on the formation of the photochemical micro-/nano-swelling of silicone rubber, our previous research was extended by examining whether the height of the growing photochemical micro-/nano-swelling before saturation could be controlled by a second ArF excimer laser with a different pulse-repetition interval. In addition, the effect of the interval was examined when the silicone rubber was heated. To examine the process of photochemical micro-/nano-swelling, an early stage of growth was observed using an atomic force microscope (AFM). We found that the photochemical micro-/nano-swelling due to the volume expansion caused by the photodissociation of Si–O bonds in the laser-irradiated area that is contacted with a silica glass microsphere is temporarily suppressed to produce a dented structure. In addition, the effect of the diffraction of the ArF excimer laser in the gaps between the silica glass microspheres on the shape of the photochemical micro-/nano-swelling was revealed when the microspheres were sparsely aligned.

## 2. Experimental Procedure

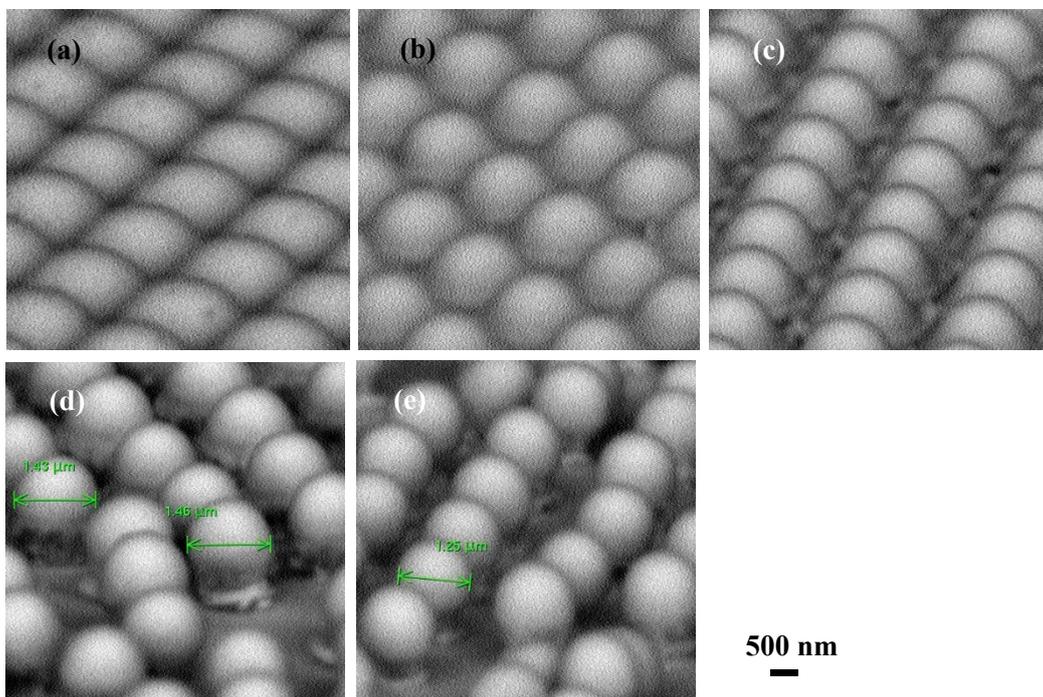
A single layer of silica glass microspheres with a diameter of approximately 2.5 μm (Nippon Shokubai, KE-P250, Osaka, Japan) was formed on 2 mm thick silicone rubber, as described in our previous paper [14]. The sample was placed 80 mm from the outlet of the ArF excimer laser (Coherent, COMPexPro110, Dieburg, Germany). The laser beam path was filled with N<sub>2</sub> gas at the flow rate of 20 L/min to avoid the strong optical absorption of oxygen molecules in the air. The ArF excimer laser irradiated the sample surface without a lens. The single pulse fluence of the ArF excimer laser was approximately 10 mJ/cm<sup>2</sup>. The pulse-repetition interval was changed by varying the laser pulse-repetition rate from 2 to 50 Hz. The laser pulse number ranged from 100 to 1800. After laser irradiation, the silica glass microspheres were removed by a 1 wt % HF chemical etching. The etching time was changed from 0 to 180 s. The pulse width of the ArF excimer laser was 20 ns. All of the laser irradiations were carried out at room temperature. To see the shape of the photochemical micro-/nano-swelling, the samples were observed using a scanning electron microscope (SEM, Phenomworld, Pro, Eindhoven, The Netherlands) and AFM (Hitachi, AFM5100N, Tokyo, Japan). The height of the micro-/nano-swelling was also measured using the AFM.

## 3. Results and Discussion

After the laser irradiation, the photochemical micro-/nano-swelling of the silicone rubber was photochemically welded to each silica glass microsphere [14] because an extremely thin layer of the micro-/nano-swelling may be photochemically modified into a silica-like silicone during laser irradiation [25]. Thus, to remove the microspheres, a 1 wt % HF chemical etching was required. Figure 1 shows the top view of the SEM images of the aligned silica glass microspheres on silicone rubber after the HF chemical etching for 0, 15, 30, 60, and 90 s. For reference, an oblique view of the SEM images is also shown in Figure 2.



**Figure 1.** A top view of the SEM images of the aligned silica glass microspheres on silicone rubber after the HF chemical etching for (a) 0, (b) 15, (c) 30, (d) 60, and (e) 90 s.

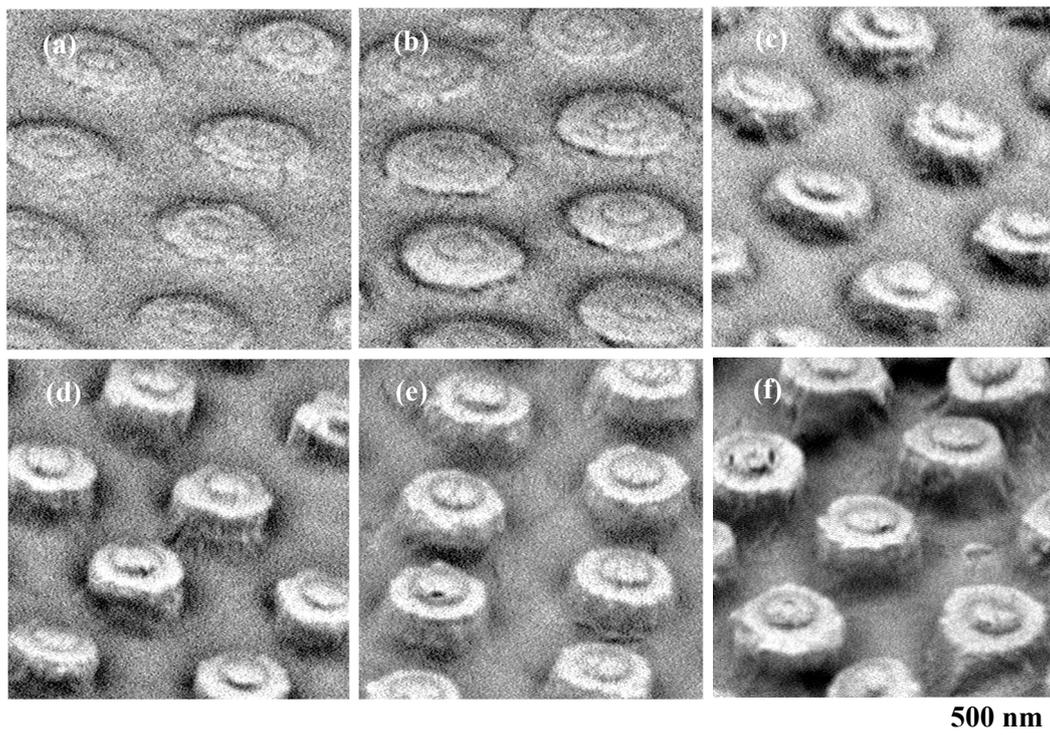


**Figure 2.** An oblique view of the SEM images of the aligned silica glass microspheres on silicone rubber after the HF chemical etching for (a) 0, (b) 15, (c) 30, (d) 60, and (e) 90 s.

These SEM images indicate that the diameter of the silica glass microspheres decreased with an increase in etching time. In the cases of 60 and 90 s, the diameters were both drastically reduced, from approximately 1.4 to 1.5  $\mu\text{m}$ . Then, at 105 s, the silica glass microspheres disappeared and were completely etched. In the actual experiment, the HF

chemical etching for 90 s was enough to remove the microspheres, successfully resulting in the photochemical micro-/nano-swelling [14].

Figure 3 shows the SEM images of the photochemical micro-/nano-swelling formed on silicone rubber after HF chemical etching. In these cases, the pulse-repetition interval was changed from 20 to 500 ms by varying the pulse-repetition rate of the ArF excimer laser from 50 to 2 Hz. In the case of 50 Hz (Figure 3a), the average height of the micro-/nano-swelling was approximately 245 nm. When the pulse-repetition rate increased to 20 Hz (Figure 3b), the average height was approximately 311 nm. On the contrary, the average height remarkably increased to approximately 588 nm when the pulse-repetition rate was 10 Hz (Figure 3c). In the cases of 6, 4, and 2 Hz (Figure 3d–f), the average heights of the micro-/nano-swelling were 673, 785 and 842 nm, respectively. Thus, a long pulse-repetition interval of equal to or greater than 100 ms effectively increases the height of the photochemical micro-/nano-swelling. When the pulse-repetition interval was 1000 ms (1 s), and the pulse-repetition rate was 1 Hz, the average height of the micro-/nano-swelling increased further to approximately 1  $\mu\text{m}$ . The case of the pulse-repetition rate of 1 Hz is not mentioned in this paper because a new phenomenon was identified that resulted in the remarkable growth of the micro-/nano-swelling. This finding is currently being examined and will be published elsewhere. In addition, because the micro-/nano-swelling is based on the photodissociation of the main chain of the polymer, the phenomenon might apply to other polymer materials.

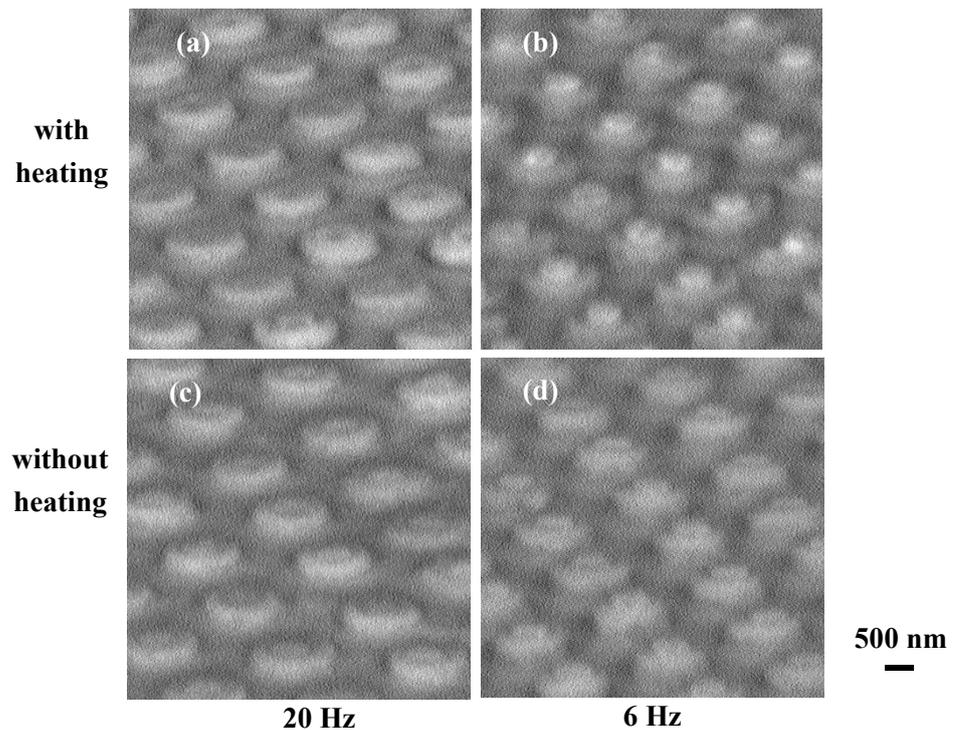


**Figure 3.** SEM images of the photochemical micro-/nano-swelling formed on silicone rubber after HF chemical etching. The pulse-repetition rate was variously set to (a) 50, (b) 20, (c) 10, (d) 6, (e) 4, and (f) 2 Hz.

In photochemical micro-/nano-swelling, the pulse energy per unit area of the ArF excimer laser is also important; increasing the pulse energy increases the diameter of the micro-/nano-swelling [15]. The interval effect is qualitatively universal in any pulse energy per unit area below the laser ablation threshold of 50  $\text{mJ}/\text{cm}^2$  [13].

To understand the effect of the pulse-repetition interval, silicone rubber was heated to 80  $^{\circ}\text{C}$  during laser irradiation. The temperature of 80  $^{\circ}\text{C}$  is not high for silicone rubber; however, if the heating results in slight warping, it would be difficult to observe the samples

using SEM; thus, the heating temperature was set to 80 °C. Figure 4 shows the SEM images of the photochemical micro-/nano-swelling formed on silicone rubber with and without heating. The pulse-repetition rate was 20 and 6 Hz. No remarkable difference in the height and shape of the micro-/nano-swelling was seen with and without the heating at both pulse-repetition rates. Therefore, it was found that the photodissociation of Si–O and Si–CH<sub>3</sub> bonds of silicone rubber induced by the ArF excimer laser was not affected by the moderate heating which did not result in plastic deformation in the cases of both 20 and 6 Hz.

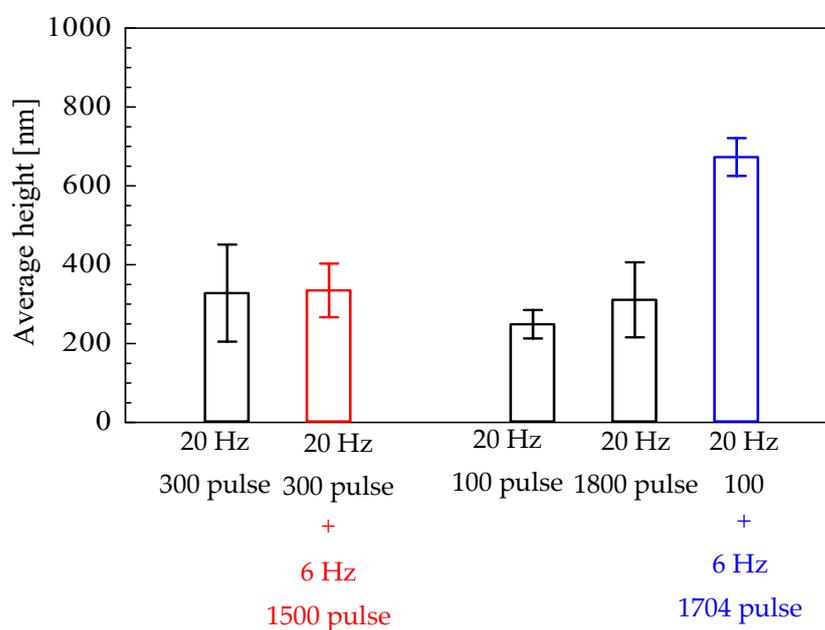


**Figure 4.** SEM images of the photochemical micro-/nano-swelling formed on silicone rubber with (a,b) and without heating (c,d) at 80 °C. The pulse-repetition rate was 20 and 6 Hz.

Moreover, to investigate the effect of the interval, we examined whether the height of the growing photochemical micro-/nano-swelling before the saturation could be controlled by a second ArF excimer laser with a different pulse-repetition interval. The results show that the height of the micro-/nano-swelling was saturated at a laser pulse number equal to or greater than 300, although each of the saturated heights of the micro-/nano-swelling formed by several pulse-repetition intervals was different. Thus, a second ArF excimer laser with a different pulse-repetition interval irradiated the growing micro-/nano-swelling before the saturation. First, as shown in Figure 5, we compared the case at 20 Hz and 300 pulses, with the case to which a second ArF excimer laser of 6 Hz and 1500 pulses was added. As a result, a difference between the two samples was not recognized. The height of the micro-/nano-swelling formed at 20 Hz and 300 pulses was saturated; thus, the second ArF excimer laser in any pulse-repetition interval could not increase the photochemical micro-/nano-swelling. In contrast, a second ArF excimer laser of 6 Hz and 1704 pulses increased the height of the micro-/nano-swelling formed at 20 Hz and 100 pulses to the saturated height of approximately 673 nm when the pulse-repetition rate was 6 Hz, which was significantly higher than that of the case of 20 Hz and 1800 pulses. Therefore, it was found that the saturated height of the increased micro-/nano-swelling could be controlled by the pulse-repetition interval of a second ArF excimer laser.

To examine the process of photochemical micro-/nano-swelling, an early stage of growing micro-/nano-swelling was observed using AFM, as shown in Figure 6. The laser pulse numbers were 50 and 900, and the pulse-repetition rate was 2 Hz. In the case of

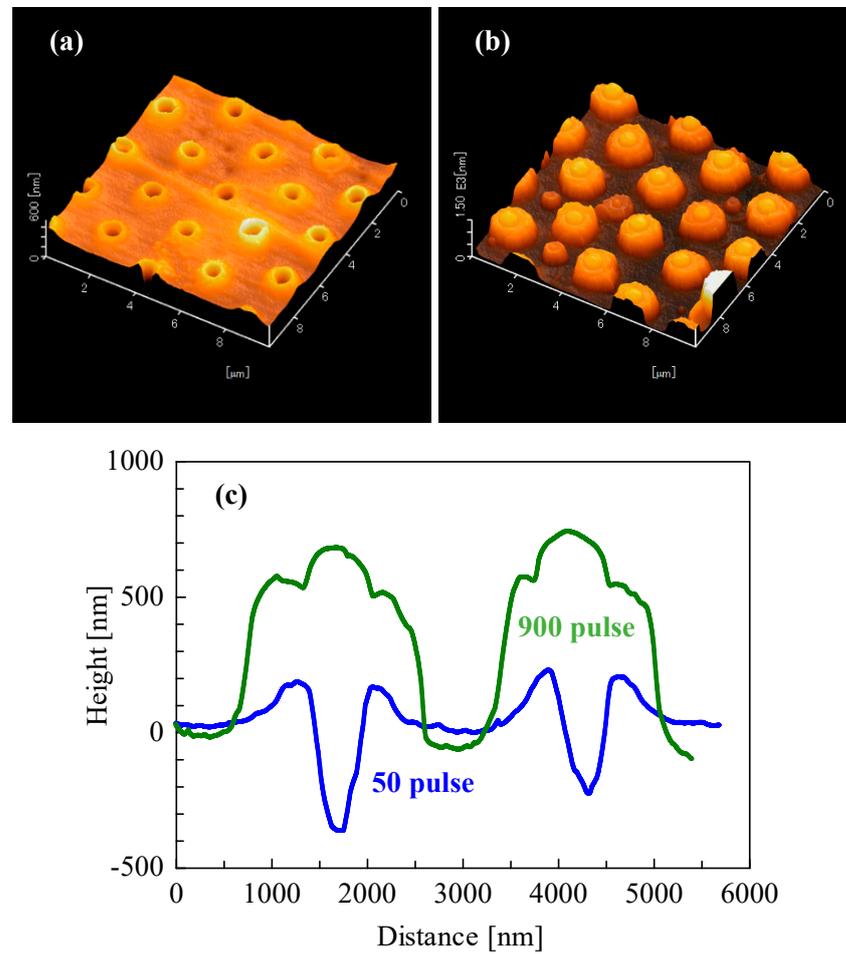
50 pulses, as shown in Figure 6a,c, a dent structure was seen. The critical number of pulses at which the dent structure disappeared seemed to be in the range of 200 to 300. When the pulse number was increased to 900, as shown in Figure 6b,c, a frusto-conical shape of the micro-/nano-swelling could be observed [14]. By analogy with these results, a dent area might be contacted with a silica glass microsphere before laser irradiation; the circular area surrounding the dent area, which is not contacted with a microsphere, might swell preferentially to form a dent structure. The Si–O bonds of silicone rubber are photodissociated by the ArF excimer laser to produce the lower molecules; therefore, these molecules might be pushed down by the microsphere, preventing the contacted area from swelling. By increasing the laser pulse number, the dent area might swell faster because the area is not temporarily in contact with the microsphere. Furthermore, this also becomes the highest fluence area due to the focusing of the ArF excimer laser, in addition to the swelling of the whole laser-irradiated area.



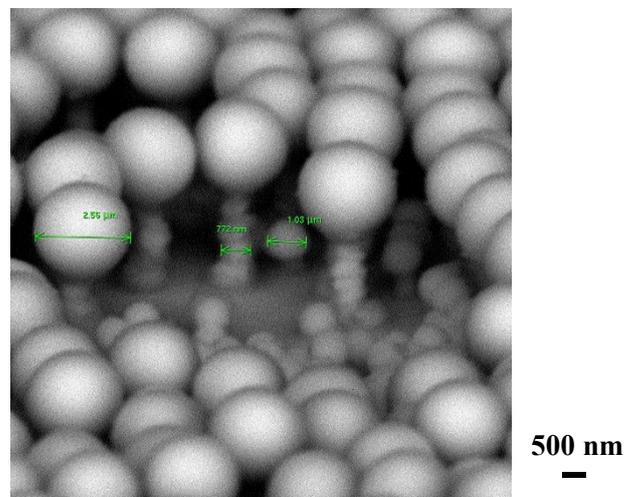
**Figure 5.** Increase in average heights of the photochemical micro-/nano-swelling formed on silicone rubber when a second ArF excimer laser at a pulse-repetition rate of 6 Hz irradiated the micro-/nano-swellings before and after the saturation.

In another approach to examining the swelling process, silica glass microspheres were sparsely aligned, which contrasts with our previous work [14]. Then, the ArF excimer laser irradiated the sample. The pulse number was 1800. Figure 7 shows the SEM image of the photochemical micro-/nano-swellings underneath silica glass microspheres before the HF chemical etching. Compared with the case in Figure 3, the width of the micro-/nano-swelling was extremely narrow and estimated to be roughly 700 nm, which is half the width obtained in Figure 3. When the microspheres were densely aligned, gaps between microspheres were very small; diffraction of the ArF excimer laser occurred, and the diffracted laser enabled the shadow areas under each microsphere to be irradiated. Thus, in our previous case, the width of micro-/nano-swelling was relatively wide, and the micro-/nano-swelling became a frusto-conical shape. In contrast, in the case of sparse alignment, the ArF excimer laser irradiated almost vertically to the surface of silicone rubber, and the shadow areas under each microsphere were not irradiated. Therefore, the ArF excimer laser could induce micro-/nano-swelling only on the focused area underneath the microsphere to produce a needle-like structure. However, at this stage, it was difficult to remove microspheres on the needle-like structure, and the needle-like structure was bent during HF chemical etching. For further formation, the HF concentration and etching

time should be adjusted in detail. The formation of the needle-like micro-/nano-swelling of silicone rubber could enhance the superhydrophobic property.



**Figure 6.** AFM images of the photochemical micro-/nano-swelling formed on silicone rubber at laser pulse numbers of (a) 50 and (b) 900, and (c) these profiles. The pulse-repetition rate was 2 Hz.



**Figure 7.** SEM image of the photochemical micro-/nano-swelling underneath silica glass microspheres before HF chemical etching when the microspheres were sparsely aligned.

#### 4. Conclusions

The height of the photochemical micro-/nano-swelling of silicone rubber was successfully increased by choosing long pulse-repetition intervals of 100 to 500 ms of an ArF excimer laser, as observed using SEM. The effect of the interval was also evident when the silicone rubber was heated to 80 °C during laser irradiation. The use of the ArF excimer laser was essential for the photochemical micro-/nano-swelling. The height of the micro-/nano-swelling was saturated at a laser pulse number equal to or greater than 300, although each of the saturated heights of the micro-/nano-swelling was formed by several pulse-repetition intervals was different. Thus, the second ArF excimer laser irradiated the growing micro-/nano-swelling before the saturation, and the saturated height of the increased micro-/nano-swelling could be controlled by the pulse-repetition interval of the second ArF excimer laser. To examine the process of micro-/nano-swelling, the early stage of the growth was observed using AFM, by which the dent structure of the micro-/nano-swelling was clearly recognized. It was found that micro-/nano-swelling caused by volume expansion due to the photodissociation of Si–O bonds in the laser-irradiated area, which was in contact with a microsphere, was temporarily suppressed. In addition, the needle-like structure of the micro-/nano-swelling could be formed when silica glass microspheres were sparsely aligned. Because photochemical micro-/nano-swelling is based on the photodissociation of the main chain of the polymer, the phenomenon may be applicable in other polymer materials. By periodically applying photochemical micro-/nano-swelling, superhydrophobicity can be achieved, thus enabling the widespread biomimetic application of silicone rubber in scientific and industrial fields. The presented results indicate the potential for the fabrication of a silicone rubber-based microdevice characterized by enhanced superhydrophobicity for electrical and electronic applications.

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**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

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**Conflicts of Interest:** The author declares no conflict of interest.

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