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High Water-repellent Sheets Prepared by Nanoimprint Process

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Nanotextured surfaces of polymer sheets with high water-repellency were fabricated by a nanoimprint process. Firstly, ultra water-repellent silica thin films were deposited on Si substrates by microwave plasma-enhanced CVD (MPECVD) using an organosilicon compound as a raw material. The surface nanotextures of the film was controlled by changing deposition pressure. Secondly, the surface nanotextures of the film were imprinted into Ni molds by electroforming. Lastly, polystyrene (PS) or Silicone rubber was coated on the Ni molds by spin coating, and then the nanotextured PS (Silicone rubber) replicas have been fabricated by this process. The contact angles of the nanotextured surface of PS replicas were 140 °, while the angles for PS flat surface were 90 °.
Key words: Ultra water-repellency, nanotexture replica, microwave plasma-enhanced CVD, plastic films.

1. INTRODUCTION

In nature, water-repellent leaves such as lotus and taro exhibit various surface sculptures, mainly epiticular wax crystals in combination with papillose epidermal cells. Their contact angles to water exceed 150°, which is called "ultra or super water-repellency". The ultra water-repellent leaves in nature have a self-cleaning effect, it is the most important function for many micro-structured biological surfaces. If this performance can be used to prepare artificial surfaces, many technicas of applications can be appeared.

As well known, wettability of the surfaces to water is governed by two factors, i.e. surface energies and three-dimentional microgeometries of the surfaces. A substrate with a lower surface energy is more hydrophobic, namely, water-repellent. However, the surface energy is an intrinsic property of each material and, thus, ultra water-repellency is not available with lowering the surface energy alone. A proper texture is necessary to the surface for emerging ultra water-repellency. Controlling the surface geometry is essential in order to prepare ultra water-repellent surfaces. So far a wide variety of techniques have been employed to fabricate water-repellent thin films [1-20]. We have succeeded in fabricating transparent and ultra water-repellent films with a water contact angle about >150° at a temperature below 100°C based on microwave plasma-enhanced chemical vapor deposition (MWPECVD) [18]. The films consist of fine clusters synthesized through the plasma-assisted polymerization of organosilane molecules and probably have a certain surface roughness sufficient for ultra water-repellency.

However, there exist some problems among these films. For example, these films have no sufficient mechanical durability and thus the films can not apply to the practical usage in some industrial areas where water-repellent films are required to be robust. Microstructured biological surfaces show very fragile structures and may be easily destroyed by mechanical abrasion. If the destroy is not very serious, it can be recovered by itself. However, when the ultra water-repellent structure prepared artificially is destroyed, a reproduction cannot be performed like the nature life. If we can prepare the surface structure with ultra water-repellency by using the technology of replica, a low cost process will be realized.

In this study, we first prepared ultra water-repellent silica films by microwave plasma-enhanced CVD (MPECVD) on Si substrates. Surfaces with about ~ 300 nm microscopical roughness were formed by controlling total deposition pressures of an organosilicon gas and Ar gas. Secondly, the surface nanotextures of the ultra water-repellent films were replicated on Ni molds by electroforming. Thirdly, polystyrene (PS) (or Silicone rubber) was coated by spin coating or these sheets on the Ni molds, and then the nanotextured PS replicas were fabricated.

2. EXPERIMENTAL METHODS

Figure 1 shows the nanoimprint process of nanotexture replica prepared in this study. This process has three steps. In Step 1, a nanotextured film with ultra water-repellency was prepared by MPECVD. The MPECVD system consisted of a Vycor glass discharge tube attached with a microwave cavity and a deposition

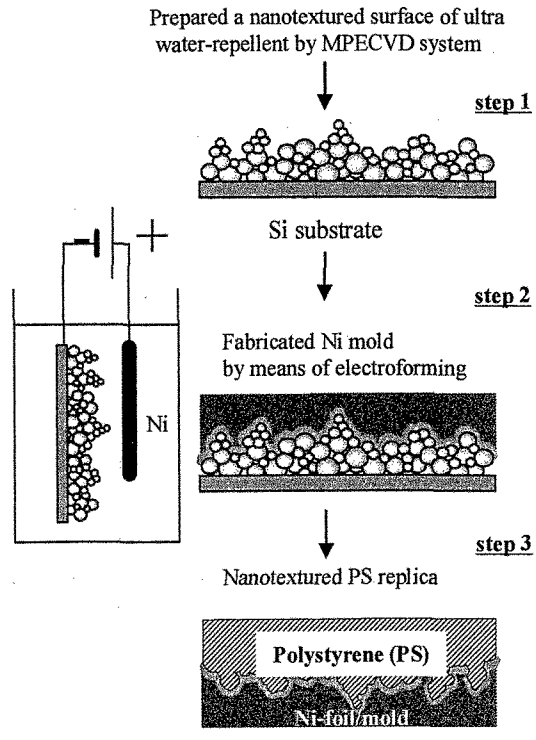

Fig. 1. Nanotexture replica process.

chamber made of stainless steel [18]. A 2.45 GHz generator supplied microwave with a power of 300 W. A Si substrate was located at the position more than 40 cm apart from the center of the plasma. The material used was a gas mixture of trimetylmethoxysilane (TMMOS; $(CH_3)_3SiOCH_3$) and Ar. During deposition for 5 min, the substrate temperature remained below 373 K. Under proper conditions, the TMMOS molecules were decomposed and aggregated in the plasma so as to form a film with ultra water-repellency which had a nanotextured surface. Changing the total pressure, various surface nanotextures were formed and the water contact angle varied.

In Step 2, using the ultra water-repellent film as a template, Ni mold was fabricated by Ni electroforming. In order to attain electric conductivity, the ultra water-repellent film was coated with a Pt layer of 10 nm thick by sputtering for 100 s. Electroforming was conducted in a constant potential mode. A DC voltage of 18 V was applied between the sample and a counter Ni electrode, which served as cathode and anode, respectively.

In Step 3, the replica of polystyrene (PS) and Silicone rubber were made from the Ni mold with surface nanotextures. First, the polymers were spin-coated on the Ni mold. The polymers sheets were separated from the Ni mold by heating at (323 ~ 373 K). This experiment was conducted at room temperature under atmospheric pressure. Secondly, the flat polymer sheet placing on the Ni mold was heated and pressed on Ni mold.

The water repellency of the polymers replicas was evaluated by measuring the water-contact-angle. Water contact angles of the replicas were measured with a contact angle meter (Kyowa Interface Science, CA-D) based on the sessile water drop method with a water drop of 2 mm in diameter. The measurements of the molds were observed with a field emission scanning electron microscope (FE-SEM; JEOL, JSM-6330F) at an accelerating voltage in the range of 5 – 10 keV. The value of root mean square roughness (R_{rms}) of the films was measured in a non-contact mode with an atomic force microscope (AFM; Seiko Instruments, SPA-300HV+SPI-3800N). A Si cantilever (Nanosensors; radius of curvature less than 15 nm) was used. Images were recorded with a typical scan speed of 0.5 Hz in the areas of 10 μm × 10 μm.

3. RESULTS AND DISCUSSION

Nanotextured surfaces were prepared by using MPECVD with different deposition pressures. We observed the nanotextured surfaces by FE-SEM such as Figs. 2 (a) ~ (c), the FE-SEM images of those surfaces shows that the surface morphology alters clearly with different total pressures. The thin films deposited at higher total pressures were composed of fine particles of several tens of nanometers, and had rough microstructure with pores of ca. 30 ~ nm. The films with irregular surface topography have the capability of ultra water-repellency. These films have a particular nanotexture which consisted of nano-scale pores between columns of a few hundreds nm in diameter.

In order to replicate ultra water-repellent surface structure, we prepared Ni mold (in the Step 2) using those samples with the ultra water-repellency.

The surface of a prepared Ni mold is shown in Figs. 2 (d) ~ (f). With the increase of surface roughness, nickel mold surface became coarse. However, the part of sample c with small unevenness can not replicate completely. It is considered that

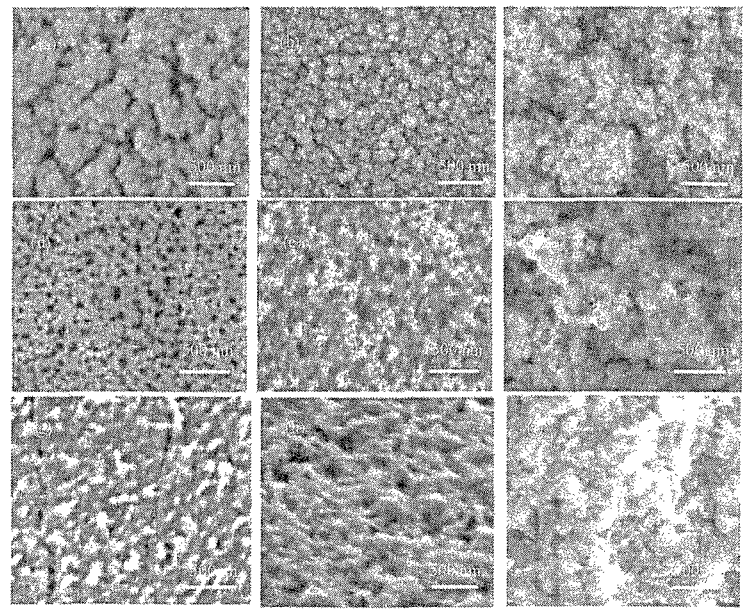

Fig. 2. FE-SEM images
(a) ~ (c) is nanotextured surfaces prepared by MPECVD with different deposition pressures
(a); deposition pressure: 50 Pa, water contact angle:150 degrees.
Roughness of surfaces (Rrms) was 30~40 nm
(b); deposition pressure: 80 Pa, water contact angle: more than150 degrees.
Roughness of surfaces (Rrms) was 50~70 nm
(c); deposition pressure: 130 Pa, water contact angle: more than150 degrees.
Roughness of surfaces (Rrms) was 80~ nm
(d) ~ (f) are the surface of fabricated Ni molds by electroforming
(d) by sample (a)
(e) by sample (b)
(f) by sample (c)
(g) ~ (i) are replication of PS by spin-coating and it dries at 373K.
(g) by Ni mold (d), contact angle is 120 degrees.
(h) by Ni mold (e), contact angle is 130 degrees.
(i) by Ni mold (f), contact angle is 110 degrees.

when sample c is put into Ni electroforming solution, the fine particle will exfoliated from the surface since the mechanical properties of the surface is weak.

The thickness of the nickel mold is about 0.5 mm. The cross-sectional photograph (Fig. 3 (b)) shows that there exist nanotextures about 200 nm and a fine nano-structure has been replicated on the Ni mold.

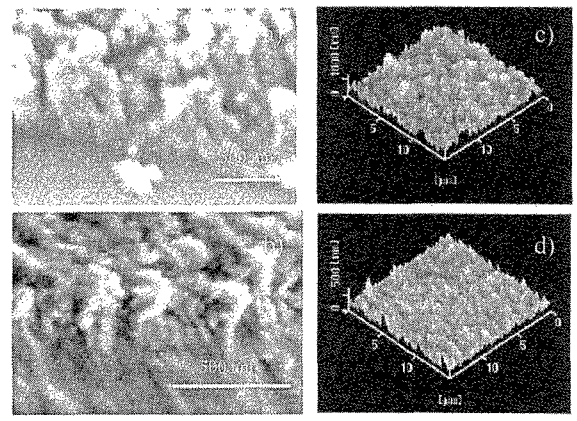

Fig. 3. Images of the cross-section and the surface by FE-SEM and AFM.
(a), (c) are the cross-section and surface of the ultra water-repellent films.
(b), (d) are the cross-section and surface of fabricated Ni mold by using the sample (b) (Fig. 2(b)) via electroforming.

Nickel mold surface showed that there was much needlelike concavo-convex form from the AFM image (Fig. 3 (c) and (d)). This can be thought that the deep place of the surface of the ultra

water-repellent sample was transferred. The thickness of the thin film was about ~ 600 nm. A surface height difference of the film

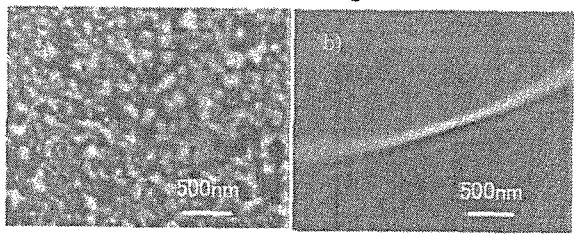

Fig. 4. Nanotextured PS replica and water repellency.
(a) PS replica by using Ni mold (Fig.2 (e)), water contact angle:140 degrees.
(b) PS replica by using non-nanotextured surface (glass). water contact angle: 90 degrees.

is about 400nm by AFM method. The rate of transfer was obtained about 50% by the results of the FE-SEM image and AFM. For an irregular structure reason, the rate of transfer of nickel mold is not obtained correctly.

A PS sheet obtained by removing the Ni mold was transparent and the thickness was about 1 mm. The surface structure of the transferred PS is shown in Fig. 2 (g) ~ (i). The of all samples is bigger than that of the flat surface (90 °). The biggest contact angle is about 130 degrees. The surface nanotexture is confirmed to be replicated by our process and is certainly effective to increase water repellency. From FE-SEM photographs, it was shown that the coarseness of the surface of the PS sheet became small compared with the original surface. Moreover, the convex portion is big and thick. Since PS was not pressed in the transfer process, it can be considered that the

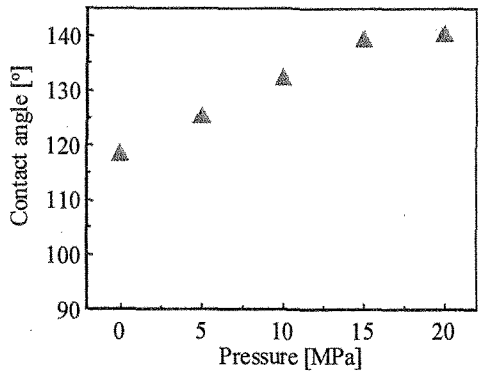

Fig. 5 The contact angle of PS sheet produced according to different press conditions at 373K.

nano-structure have been not transferred to PS completely. In the case of silicone rubber because it cannot be removed completely, a process needs to be improved.

The surface naotextures of the PS replica and the flat PS sheets in the second test are shown in Fig.4. Fig. 4(b) is the surface of the flat PS sheet, its contact angle is about 90-95 °.

From Fig. 5, it was shown that the contact angle increased with the pressure increasing. The surface of the pressed sample has more bigger convex structure. The contact angle was 140 degrees. The contact angle was almost unchanged when the pressure was set to 15 MPa or more because the nickel mold can not replica inadequately in the condition.

The result of the silicone rubber replicated indicated that the contact angel of the replicated surface became bigger compared with flat silicone rubber surface. But the replicated silicon rubber sheet is difficult to separated from the Ni mold. It need further study in the future.

4. CONCLUSIONS

We have successfully replicated the surface nanotextures get from the plasma CVD method on the surface of Polymer. The transparent and high water-repellency sheet can be produced by nanoimprint process. The electroforming is an effective way to duplicate minute structures in nanometer scale. Because the Ni mold can be used repeatedly, our nanoimprint process will has a bright foreground in the production of plastic films with high water-repellency.

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