Surface modification of PDMS by atmospheric-pressure plasma-enhanced chemical vapor deposition and analysis of long-lasting surface hydrophilicity

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\textbf{A B S T R A C T}

Atmospheric-pressure plasma-enhanced chemical vapor deposition (AP-PECVD) offers several benefits such as simplicity, high productivity, and versatility. An AP-PECVD-based method is proposed in this study to modify hydrophobic PDMS (polydimethylsiloxane) surfaces towards a long-lasting hydrophilic character. To enhance the sustainability of the hydrophilicity, two kinds of layers were sequentially deposited by AP-PECVD on the surface of a PDMS block (TEOS-O\textsubscript{2}/CH\textsubscript{4}/PDMS). A hydrocarbon layer was first coated on the bare PDMS surface using CH\textsubscript{4} as the reactant, and then, a hydrophilic SiO\textsubscript{x} layer was deposited using tetraethyl orthosilicate and oxygen (TEOS-O\textsubscript{2}). The highly cross-linked hydrocarbon layer acted as a physical barrier layer (PBL) between the bare PDMS surface and the hydrophilic layer. To confirm that the PBL suppresses the hydrophobic recovery of the modified PDMS surface with double layer, a single-layer-coated PDMS sample (TEOS-O\textsubscript{2}/PDMS) without the PBL was prepared by AP-PECVD using TEOS-O\textsubscript{2}. The surface characteristics were determined by static contact angle measurements, surface roughness measurements, and surface chemical composition/chemical bonding determination and compared with those of modified PDMS surface with double layer. The surface morphology of TEOS-O\textsubscript{2}/PDMS degraded seriously by the diffusion of PDMS oligomers to the hydrophilic layer, but that of TEOS-O\textsubscript{2}/CH\textsubscript{4}/PDMS was sustained for a long time. Thus, TEOS-O\textsubscript{2}/CH\textsubscript{4}/PDMS has the lowest contact angle, almost 0\degree, and showed long-lasting surface hydrophilicity, with almost no change in the contact angle for 28 days. Thus, this proposed method is confirmed to be well suited for use in applications that require stable hydrophilic surface property in PDMS.

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1. Introduction

Polydimethylsiloxane (PDMS) is widely used for the microfabrication of various lab-on-a-chip devices because it is inexpensive, biocompatible, self-sealable, and highly elastic; further, it has excellent optical transparency and allows for easy device fabrication [1,2]. However, because of its innate hydrophobicity, PDMS shows nonspecific binding with biomolecules via physical adsorption [3] and has limited electro-osmotic flow applications [4]. Furthermore, an external mechanical or electrical power source is required, in general, to support the transport of liquids in a PDMS-based lab-on-a-chip system [5].

Attempts have been made to make the PDMS surface hydrophilic by surface modification, while preserving the bulk-material properties [4–6]. Oxygen-based plasma treatment is a simple and commonly used means of making the PDMS surface hydrophilic, but the hydrophilicity is soon lost because PDMS oligomers migrating from the bulk to the air-surface interface cause hydrophobic recovery within a few hours following the plasma treatment [4,7]. Storing PDMS under water after oxygen-based plasma treatment can reduce the rate of hydrophobic recovery, but this method of storage is not applicable to PDMS-based microfluidic devices [2,8,9]. Thus, increasing the hydrophilicity to the maximum possible extent and preserving it for a long time even when PDMS is stored under dry conditions is critical issues. In addition, the surface modification procedure to be chosen should be simple and cost-effective so that it can be used for large-scale surface modification. Numerous methods such as thermal aging [10], sol–gel coating [11], deliberate protein adsorption [12], layer-by-layer (LBL) deposition [13], silanization [14], and

\textit{Abbreviations}: AP-PECVD, atmospheric-pressure plasma-enhanced chemical vapor deposition; PDMS, polydimethylsiloxane; TEOS, tetraethyl orthosilicate; PBL, physical barrier layer; LBL, layer-by-layer; PPAA, plasma polymerized acrylic acid; RF, radiofrequency; DOE, design of study; ANOVA, analysis of variance; XPS, X-ray photoelectron spectroscopy; SEM, scanning electron microscopy.

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radiation-induced graft polymerization [7,15,16] have been proposed for achieving long-term surface hydrophilicity. Moreover, to inhibit the migration of PDMS oligomers from the bulk to the surface, the physical barrier layer (PBL) concept has been introduced in various surface modification methods such as UV polymerization [17], silanization [18], and chemical vapor deposition (CVD) [19,20]. Plasma polymerization has been used for the surface modification of PDMS by the deposition of a PBL such as a plasma polymerized acrylic acid (PPAA) layer [19]. The wettability and hydrophilicity of the PDMS surface modified using these PBL-based methods are retained for a long time, and the rate of hydrophobic recovery is efficiently decreased [4]. Currently, there is a strong demand for surface modification methods that can induce surface hydrophilicity not only in PDMS but also in synthetic polymers with an inert hydrophobic surface [21,22].

Plasma polymerization that includes plasma-enhanced chemical vapor deposition (PECVD) is widely used for surface modification and thin-film fabrication since it is a gas-phase process in which chemical wastes are not produced, and therefore, washing and drying steps are not necessary. Furthermore, the deposition layer in PECVD can be changed by simply changing the reactant, similar to the case of chemical polymerization, where the nature of the product can be varied by changing the monomer used. Recently, atmospheric-pressure PECVD (AP-PECVD), in which plasma deposition is effected at atmospheric pressure, has gained popularity [23–25]. Since the AP-PECVD apparatus can be operated at atmospheric pressure, no vacuum chamber or pumping system is required; further, there is no limit on the substrate size to be used in AP-PECVD, as opposed to low-pressure plasma-enhanced chemical vapor deposition, in which only small substrates can be employed. In addition, AP-PECVD allows for parallel and in-line processing [26–28].

A stable hydrophobic layer on hydrophilic materials has been previously developed by depositing a hydrocarbon layer on the substrate by AP-PECVD using CH₄ as the reactant [29]. Plasma polymerization yields a highly cross-linked layer by promoting random chemical reactions between various radicals activated by the radiofrequency (RF) plasma in the polymerization step, and the hydrophobicity of the coating layer is retained for more than 4 months. In addition, SiOₓ or SiOC layers can be deposited by AP-PECVD using tetraethyl orthosilicate (TEOS) with/without O₂ [24,30,31]. The SiOₓ layer is strongly hydrophilic, and hence, it can be used to make the PDMS surface hydrophilic.

In this study, we developed a method for making the hydrophobic PDMS surface hydrophilic by surface modification and ensuring long-lasting hydrophilicity. Two layers were sequentially deposited on a PDMS block via AP-PECVD using CH₄ and TEOS-O₂ reactants. A PBL, the lower layer in the double layer, was first deposited on the bare PDMS surface by using CH₄ as the reactant, and then, a highly hydrophilic layer, the upper layer, was deposited using TEOS-O₂ as the reactant. The combination of two functional layers deposited by AP-PECVD helps in achieving long-lasting hydrophilicity on the PDMS surface, and this double-layer deposition is simple and rapid. On the basis of the idea of surface modification, the optimal processing conditions for double-layer deposition through AP-PECVD were investigated by monitoring the static contact angle, which is related to the rate of hydrophobic recovery. To compare the long-term hydrophilicity after surface modification, four PDMS samples—unmodified PDMS sample, two PDMS samples modified by single-layer deposition (CH₄/PDMS, TEOS-O₂/PDMS), and the PDMS sample modified by double-layer deposition (TEOS-O₂/CH₄/PDMS)—were characterized. The modified PDMS surface was characterized by surface topography analysis, static contact angle measurements, and surface chemical composition/chemical bonding determination to confirm the effectiveness of the proposed method.

2. Experimental

2.1. Materials

PDMS (prepolymer) and Sylgard 184 (curing agent) were mixed in 10:1 ratio and stirred. Then, 20-g portions of this mixture were poured into a polystyrene Petri dish, 10150 (SPL Life Science Co., Republic of Korea) to form a 1-mm-thick layer, degassed in a vacuum desiccator for removing bubbles, and cured in an oven at 80 °C for 90 min. Subsequently, the flat PDMS samples were cut into 2 cm x 4 cm pieces and peeled off.

2.2. Surface modification by AP-PECVD

For depositing each layer of the double layer, a commercial AP-PECVD system (IDP-1000; APPlasma Co., Republic of Korea) operating at an RF of 13.56 MHz was utilized. 5% of CH₄ mixed with argon was used as the reactant for the PBL deposition, while a mixture of TEOS (vaporized by 1 slm of argon) and O₂ was used for depositing the hydrophilic SiOₓ layer on the PBL. Helium was used as the carrier gas (15 slm for AP-PECVD with CH₄; 5–15 slm for AP-PECVD with TEOS-O₂). A RF power of 200 W was employed for plasma deposition. The distance between the nozzle head of the plasma source and the sample was adjusted to 1.5 mm for PBL deposition and 2 mm for the hydrophilic layer deposition. The samples were mounted on a moving stage positioned below the plasma source; the stage moved at a speed of about 20 mm/s in the orthogonal direction with respect to the plasma source head. The substrate was repeatedly repeated back and forth across the plasma head region. This surface modification on each PDMS sample could be completed within 10 min for long-lasting hydrophilicity.

2.3. Design of experiment for optimal processing conditions

The processing conditions that afford long-lasting hydrophilicity of the PDMS surface were determined by design of experiment (DOE). The optimal processing conditions for the double-layer deposition were investigated by monitoring the static contact angle on the seventh day following surface modification, which represented the rate of hydrophobic recovery of the modified surface. A DOE was performed using a standard L₁₈ orthogonal array including five factors to identify the optimal processing conditions. A number of controllable factors that may influence the characteristics of plasma deposition were selected. Five of these factors were considered the major ones affecting the wettability; two influenced only the PBL properties, and three were related to the properties of the hydrophilic layer. One of the five factors was selected to investigate the efficiency of the two reactants, CH₄ and vaporized TEOS, in acting as a PBL and inhibiting hydrophobic recovery on the modified hydrophilic PDMS surface. The first factor determined the chemical composition of the PBL. Two factors that affect the thickness of each PBL and hydrophilic layer were chosen by controlling the number of head movements in AP-PECVD. The flow rates of the carrier gas helium and O₂ in the hydrophilic layer deposition were added as factors that would determine the activation ratio of the chemical reaction and the physical bombardment in the atmospheric-pressure plasma field, which in turn influence the physical and chemical properties of the SiOₓ layer. When using L₁₈ orthogonal array, only 18 cases were required under each set of processing conditions, for accurately evaluating the contribution of each factor to the contact angle. A balanced level of each factor was assigned to each trial, the L₁₈ orthogonal array was constructed, and two PDMS samples were considered for each set of
processing conditions. The main effects of the factors were evaluated on the basis of a general linear model analysis of variance (ANOVA).

2.4. Surface analysis of modified PDMS sample

Static contact angles were measured in a Phoenix 300 apparatus (SEO Co., Republic of Korea) using deionized water. A 4-μl droplet of deionized water was added to the sample surface by controlled injection. The topography of the modified PDMS surface was characterized by using a Hitachi S-4700 scanning electron microscope at an acceleration voltage of 10 kV. Prior to the imaging process, all the samples were sputter-coated with platinum for a period of 65 s. To validate the optimal conditions and investigate the effect of hydrophobic recovery over a long time, static contact angle measurements and SEM images were performed at two points each on the surface of three fresh samples on day 0, 7, 14, and 28 after surface modification. The PDMS samples were stored for 28 days at room temperature in a clean room with 30% relative humidity.

X-ray photoelectron spectroscopy (XPS) analysis of the surface composition was carried out 3 days after surface modification, using a MultiLab 2000 instrument (Thermo Electron Corp., MA, US) with an Al-Kα X-ray source. The analyzed core-level lines (C 1s, Si 2p) were calibrated with respect to the C 1s binding energy set at 285 eV. Changes in the chemical bonds on the modified PDMS surfaces were examined by refining the C and Si peaks.

UV–VIS transmission spectra were measured using a Cary 5000 spectrophotometer (Varian Inc., Australia) to determine the transmittance of the modified PDMS sample with double layer comparing with those of unmodified PDMS sample.

To measure the thickness of the PBL according to the number of head movements in applying AP-PECVD using CH₄, one-half of the PDMS surface was blocked by a cover slip, and a CH₄ layer (PBL) was deposited by AP-PECVD on the exposed area. After the cover slip was removed, the thickness of the PBL was estimated from the height of the PBL measured by an optical 3D profiler, μSurf (NanoFocus AG, Germany).

### 3. Results and discussion

#### 3.1. Surface properties of modified PDMS samples

SEM images of the PDMS surfaces are shown in Fig. 1, with the static contact angle images measured on the day of surface modification. The hydrophobic surfaces of the unmodified PDMS and CH₄/PDMS samples were smoother than those of the hydrophilic TEOS-O₂/PDMS and TEOS-O₂/CH₄/PDMS samples; this was because the TEOS-O₂ coating layer comprised hydrophilic SiOₓ particles, which made the surface rough in the latter two samples [24].

Fig. 2 shows the XPS results before and after plasma treatment. The marked increase in the intensity of the O 1s peak and the moderate increase in the intensities of the Si 2s and Si 2p peaks were due to the deposition of the hydrophilic SiOₓ layer generated by AP-PECVD using TEOS-O₂ (Fig. 2(c) and (d)). However, the intensity of the C 1s peak was the highest for CH₄/PDMS (Fig. 2(b)) since only the hydrocarbon layer was deposited. A quantitative analysis of these results is shown in Table 1, including the sur-

![Fig. 1](image1.png)  
(a) unmodified PDMS, (b) CH₄/PDMS, (c) TEOS-O₂/PDMS, and (d) TEOS-O₂/CH₄/PDMS. The PDMS surface could be made hydrophilic by AP-PECVD using TEOS-O₂.

![Fig. 2](image2.png)  
XPS survey spectra: (a) unmodified PDMS, (b) CH₄/PDMS, (c) TEOS-O₂/PDMS, and (d) TEOS-O₂/CH₄/PDMS. The chemical composition differed with the precursor used in AP-PECVD.
face chemical composition and the relative percentages of bonds to the C 1s and Si 2p peaks. Table 1(a) shows that the atomic percentage of oxygen increased sharply from 27.2% in the unmodified PDMS to 44.8% in TEOS-O2/PDMS and from 27.2% to 47.1% in TEOS-O2/CH4/PDMS; however, there was a little decrease in the atomic percentage of oxygen in CH4/PDMS compared with unmodified PDMS. Moreover, the O/C ratio and O/Si ratio increased abruptly in the TEOS-O2/PDMS and TEOS-O2/CH4/PDMS samples containing SiO2 layer in common. Considering the hydrophilic surface property of these two modified PDMS samples (Fig. 1(c) and (d); contact angle images), these observations confirmed that the hydrophilicity of the modified PDMS surface was due to the incorporation of oxygen-containing groups on the surface.

Refinement of the C 1s and Si 2p peaks in the XPS spectra revealed that these elements existed in two different chemical states (see Table 1(b)). The C 1s peak was fitted to C–C– and C–O– bonds, while the Si 2p peak was fitted to silicone (C3–Si–O and C2–Si–O2) and silicate (C–Si–O3 and Si–O4) bonds [32–34]. During AP-PECVD, the concentrations of different C and Si species on the PDMS surface changed owing to the bond scission resulting from the bombardment of ionized radicals or electrons and the consequent random reactions between the various formed ionized radicals. The C–C– (C1, 284.6 eV) groups were greater in number than the C–O– (C2, 286.3 eV) groups on all the PDMS surfaces considered (Fig. 3). –C≡C– and –C–O– groups have no influence on the wettability, but the C=C– group contributes in a greater extent to surface hydrophilicity than does the –C–O– group [21]. However, in this study, the –C–O– content of the TEOS-O2/PDMS sample increased only, and –C≡C– groups were hardly detected on any PDMS surface. Fig. 4 shows that the surfaces of the unmodified PDMS and CH4/PDMS contain about 70% silicone (102.4 eV) and 30% silicate (103.7 eV). The silicone-silicate ratio on the PDMS surface reversed after surface modification by AP-PECVD with TEOS-O2 (TEOS-O2/PDMS and TEOS-O2/CH4/PDMS): the silicate content became four times higher than the silicone content (see Table 1(b)). Because of the negative electrical polarity of the chemical bonds, the silicate group is more hydrophilic than silicone, and hence, a silicate-rich surface would be highly hydrophilic. Thus, silicate-silicone ratio is the major factor determining the surface hydrophilicity of PDMS modified by AP-PECVD using TEOS-O2.

The surface layer deposited by AP-PECVD with TEOS-O2 becomes highly rough because of the presence of hydrophilic

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Table 1

<table>
<thead>
<tr>
<th>Chemical composition (At %)</th>
<th>Chemical bonds (area %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Unmodified PDMS</td>
<td>44.9</td>
</tr>
<tr>
<td>CH4/PDMS</td>
<td>57.3</td>
</tr>
<tr>
<td>TEOS-O2/PDMS</td>
<td>23.4</td>
</tr>
<tr>
<td>TEOS-O2/CH4/PDMS</td>
<td>20.7</td>
</tr>
</tbody>
</table>

Estimated chemical bonds


Fig. 3. XPS narrow spectra for C 1s: (a) unmodified PDMS, (b) CH4/PDMS, (c) TEOS-O2/PDMS, and (d) TEOS-O2/CH4/PDMS.
chemical groups and the high hydrophilicity of the modified PDMS surfaces (Fig. 1(c) and (d); contact angle images) can be explained by introducing the Wenzel model. The Wenzel model describes the contact angles on nanostructured surfaces as those according to:

$$\cos \theta^* = r \cos \theta$$

where $\theta^*$ is the apparent contact angle; $r$, the roughness ratio, i.e., the ratio of the true contact area to the apparent area; and $\theta$, the Young contact angle as defined for an ideal surface [35,36].

Summarizing the characterization data for the modified PDMS surfaces, it can be qualitatively determined that the high roughness (Fig. 1(c) and (d); SEM image) of the hydrophilic SiO$_x$ layer (Table 1(b)) deposited by AP-PECVD using TEOS-O$_2$ made the modified PDMS surface extremely hydrophilic, i.e., the contact angle was nearly $0^\circ$.

3.2. Aging effect on the modified PDMS surfaces

To monitor the change in the wettability and thus evaluate the sustainability of the surface hydrophilicity, the static contact angles on the PDMS surfaces were measured over a period of 28 days after AP-PECVD. Fig. 5 shows the representative static contact angle images recorded 0, 7, 14, and 28 days after surface modification for our PDMS samples. The contact angle on the unmodified PDMS surface was the highest (100.9$^\circ$), and that on the CH$_4$/PDMS surface was slightly lower (79.7$^\circ$); however, the TEOS-O$_2$/PDMS and TEOS-O$_2$/CH$_4$/PDMS samples had highly hydrophilic surfaces, with the static contact angle being almost $0^\circ$. Thus, we confirmed that the hydrophilic SiO$_x$ layer formed by AP-PECVD using TEOS-O$_2$ makes the PDMS surface hydrophilic on the day of surface modification, regardless of the existence of the PBL. The contact angle remained almost unchanged in the case of the unmodified PDMS and CH$_4$/PDMS but increased drastically in the case of TEOS-O$_2$/PDMS (from 0$^\circ$ to about 113$^\circ$) for 28 days. However, the contact angle remained close to 0$^\circ$ in the case of TEOS-O$_2$/CH$_4$/PDMS, indicating that the PBL helped in preserving the hydrophilicity of the modified PDMS surface by preventing hydrophobic recovery. The PDMS oligomers cannot easily penetrate the highly cross-linked hydrocarbon layer formed by AP-PECVD using CH$_4$; in other words, the PBL prevents hydrophilicity degradation that may result from the diffusion of PDMS oligomers. As shown in Fig. 6(a), the slight change in the contact angle on the CH$_4$/PDMS and TEOS-O$_2$/CH$_4$/PDMS surfaces and the steady increase in the contact angle on the TEOS-O$_2$/PDMS surface over 28 days indicated that the hydrophobic recovery in the latter case was due to the absence of the PBL. The proposed surface modification method affords much higher sustainability of the surface hydrophilicity (over 28 days) than the previously reported methods (Fig. 6(b)).

The changes in the surface roughness with aging time are shown in Fig. 7 for the TEOS-O$_2$/PDMS and TEOS-O$_2$/CH$_4$/PDMS samples. The influence of the PBL on the modified PDMS surfaces was also investigated by monitoring the surface roughness 0, 7, 14, and 28 days after surface modification. The surface topography of the two samples was initially almost identical but changed with time. Degradation of the surface roughness in TEOS-O$_2$/PDMS was observed, as shown in Fig. 7(a), because of the presence of the bulky PDMS oligomers, which gradually surrounded the hydrophilic SiO$_x$ layer, resulting in loss of hydrophilicity. However, Fig. 7(b) shows that the surface topography of TEOS-O$_2$/CH$_4$/PDMS hardly changed and no bulky PDMS oligomers were detected on the hydrophilic SiO$_x$ layer during the aging time of 28 days. Considering the chemical composition/bonding of modified PDMS surfaces and the change in surface topography during the aging time of 28 days, the surface concentration of the PDMS molecules (hydrophobic material) and SiO$_x$ (hydrophilic material) was probably responsible for the variation in the observed wettability on the modified PDMS surfaces during the aging time. In addition, the change in
the surface topography with aging had a notable effect on the contact angle resulting from the change in the roughness ratio in the Wenzel model. Thus, the decrease in the surface area of the SiO$_x$ particles and the change in the surface topography contributed to the hydrophobic recovery of the TEOS-O$_2$/PDMS surface. However, the hydrophilicity of the TEOS-O$_2$/CH$_4$/PDMS surface could be completely preserved during the aging time without hydrophobic recovery since the initial hydrophilic SiO$_x$ layer was protected from the diffusion of PDMS oligomers by the PBL formed between the PDMS surface and the hydrophilic SiO$_x$ layer.

3.3. DOE study to identify optimal processing conditions for obtaining hydrophilic PDMS surface

For identifying the optimal processing conditions under which long-lasting hydrophilicity can be achieved by double-layer deposition (via AP-PECVD), a DOE was performed under various conditions. A standard $L_{18}$ orthogonal array, which consists of five factors with two (Factor A only) or three (Factors B, C, D, E) levels, was adopted. A number of controllable factors that may influence the characteristics of the plasma deposition were selected. Five of these factors were considered the major ones affecting the wettability; two influenced only the PBL, and three were relevant to the hydrophilic SiO$_x$ layer (see Table 2).

Factor A was selected to investigate the efficiency of the two reactants in inhibiting hydrophobic recovery on the modified hydrophilic PDMS surface. Each layer of hydrocarbon or SiOC was deposited by AP-PECVD using CH$_4$ or vaporized TEOS as the reactants, respectively; hence, Factor A determined the chemical composition of the PBL. Factors B and E affected the thickness of the deposited PBL and hydrophilic SiO$_x$ layers. Factors C and D determined the activation ratio of the chemical reaction and the physical bombardment in the atmospheric-pressure plasma field, which influenced the composition of the hydrophilic SiO$_x$ layer.

![Fig. 5. Representative images of static contact angle on PDMS surfaces 0, 7, 14, and 28 days after surface modification: (a) unmodified PDMS, (b) CH$_4$/PDMS, (c) TEOS-O$_2$/PDMS, and (d) TEOS-O$_2$/CH$_4$/PDMS. The TEOS-O$_2$/PDMS surface without the PBL showed hydrophobic recovery, but the TEOS-O$_2$/CH$_4$/PDMS surface with the PBL showed long-lasting hydrophilicity.](image)

![Fig. 6. Static contact angle measured 0, 7, 14, and 28 days after surface modification: (a) comparison of unmodified PDMS, CH$_4$/PDMS, TEOS-O$_2$/PDMS, and TEOS-O$_2$/CH$_4$/PDMS; (b) comparison of results for TEOS-O$_2$/CH$_4$/PDMS with those of previous studies. The TEOS-O$_2$/CH$_4$/PDMS surface in this study showed very long-lasting hydrophilicity.](image)
Each processing condition based on the L₁₈ orthogonal array and the averaged contact angles are shown in Table 3.

The main effects of the factors for the static contact angle on the seventh day were evaluated from the experimental results (see Table 4). A general linear model ANOVA was used, and the contribution of each factor was investigated, as shown in Table 4(a). The variance of A (reactant for the first layer, PBL) had the most significant effect on the contact angle variance; thus, the optimal processing conditions when using CH₄ as the reactant gas in AP-PECVD had to be determined. Only Runs 1–9 were considered to decide the optimal processing conditions from the L₁₈ orthogonal array, and the latter 9 runs, in which factor A was TEOS (Runs 10–18), as shown in Table 4(b), were excluded. Therefore, the optimal combination of factor levels for efficient PDMS surface modification (for achieving the maximum hydrophilicity) was A₁–B₃–C₂–D₁–E₃. For validating this combination, the contact angle was measured 7 days after surface modification, as shown in Fig. 8. The results showed that the contact angle was almost 0°, which was smaller than the other contact angles obtained in the 18 trials listed in Table 3. This confirmed the validity of the optimal processing combination for obtaining the most hydrophilic PDMS surface by AP-PECVD.

Fig. 9 presents the thickness of the hydrocarbon layer deposited by AP-PECVD using CH₄ as a function of the number of head movements on the PDMS samples. The average deposition rate was almost 3 nm per head movement. Considering factor B from ANOVA, in the case of level 3 (number of head movements: 90), where the thickest PBL was deposited, the static contact angle was the lowest. However, there was no linear correlation between the PBL thickness and the static contact angle, implying that there could be some interaction between the factors. To clarify this interaction effect, an additional DOE study with a two-level factorial design would be required. However, because the optimal combination of the double layer yielded the most hydrophilic

Table 2
Factors considered in heterogeneous-double-layer deposition by atmospheric-pressure plasma for PDMS surface modification.

<table>
<thead>
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<th>Factors</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
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<td>A</td>
<td>Reactant</td>
<td>CH₄</td>
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<td></td>
<td>B</td>
<td>No. of head movements</td>
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<td>Processing conditions for the hydrophilic layer</td>
<td>C</td>
<td>O₂ flow rate</td>
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<td></td>
<td>D</td>
<td>He flow rate</td>
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<td></td>
<td>E</td>
<td>No. of head movements</td>
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Table 3
Processing conditions with L₁₈ orthogonal array and static contact angle measurement results.

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<th>E (No.)</th>
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<td>B (No.)</td>
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<td>150</td>
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<tr>
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<tr>
<td>18</td>
<td>TEOS</td>
<td>90</td>
<td>200</td>
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Fig. 8. Sequential snapshot of a water drop (4 µl) on PDMS surface with double layer deposited under optimal processing conditions in AP-PECVD after 7 days of aging. The optimal combination enhanced the long-lasting hydrophilicity of the modified PDMS surface.

PDMS surface, investigation of the aforementioned interaction was out of scope of the present study.

To verify the influence of the double layer deposited by AP-PECVD on the optical transparency, UV–VIS transmission analysis was conducted. Fig. 9 presents the UV–VIS transmission spectra of the unmodified PDMS sample and the PDMS sample modified under the optimal processing conditions; both these samples were colorless and showed a transmission of above 95% in the visible region. The transmittance of the modified PDMS surface was lower than that of the unmodified PDMS by 10% in the 300–800-nm range. However, the results of UV–VIS transmission analysis showed that the optical transparency of PDMS was fairly well preserved even after the sequential deposition of the double layer by AP-PECVD using CH₄ and TEOS-O₂.

In terms of the self-sealing property of PDMS, permanent bonding by oxygen plasma treatment is not possible for the modified PDMS surface deposited with the double layer. To induce permanent bonding of PDMS with glass, silicon, or thermoplastics via the formation of siloxane bonds (Si–O–Si), PDMS molecules should be treated by oxygen plasma to produce silanol (Si–OH) groups on their surface [2]. In the case of the PDMS sample modified by AP-PECVD, the PDMS molecules cannot be exposed to the oxygen plasma since the double layer is deposited on the bare PDMS block. To preserve the self-sealing property of PDMS for the permanent bonding of the unmodified PDMS surface with other substrates, as an alternative, selective surface modification by stencils with patternable through-holes can be adopted, and the deposition of the double layer can be selectively blocked for permanent bonding [37–39]. This approach can also be utilized to fabricate microfluidic channels.

Table 4
Main effects in DOE study of static contact angles by ANOVA for (a) full runs in L₁₈; (b) half runs from Run 1 to Run 9 (Factor A: CH₄).

(a) ANOVA for full runs in L₁₈

<table>
<thead>
<tr>
<th>Factor</th>
<th>Factor A</th>
<th>Factor B</th>
<th>Factor C</th>
<th>Factor D</th>
<th>Factor E</th>
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<tr>
<td>Level 1</td>
<td>21.18</td>
<td>51.38</td>
<td>81.37</td>
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<tr>
<td>Level 2</td>
<td>101.70</td>
<td>57.16</td>
<td>59.97</td>
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<tr>
<td>Level 3</td>
<td>–</td>
<td>75.78</td>
<td>42.98</td>
<td>77.97</td>
<td>82.56</td>
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<tr>
<td>Delta</td>
<td>80.52</td>
<td>24.41</td>
<td>38.38</td>
<td>32.81</td>
<td>41.25</td>
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<tr>
<td>Sum of Squares</td>
<td>29177.2</td>
<td>1952.2</td>
<td>202.0</td>
<td>689.0</td>
<td>1094.4</td>
</tr>
<tr>
<td>Variance</td>
<td>29177.2</td>
<td>976.1</td>
<td>60.10</td>
<td>344.5</td>
<td>547.2</td>
</tr>
<tr>
<td>Contribution</td>
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<td>2.6%</td>
<td>5.0%</td>
<td>4.3%</td>
<td>6.8%</td>
</tr>
</tbody>
</table>

(b) ANOVA for half runs (Runs 1–9)

<table>
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</thead>
<tbody>
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<td>Level 1</td>
<td>19.18</td>
<td>18.37</td>
<td>12.70</td>
<td>31.77</td>
</tr>
<tr>
<td>Level 2</td>
<td>29.33</td>
<td>18.18</td>
<td>26.00</td>
<td>16.25</td>
</tr>
<tr>
<td>Level 3</td>
<td>15.02</td>
<td>26.98</td>
<td>30.83</td>
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</tr>
<tr>
<td>Delta</td>
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<td>8.80</td>
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<tr>
<td>Sum of Squares</td>
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<td>97.0</td>
<td>105.8</td>
<td>401.2</td>
</tr>
<tr>
<td>Variance</td>
<td>162.7</td>
<td>48.5</td>
<td>52.9</td>
<td>200.6</td>
</tr>
<tr>
<td>Contribution</td>
<td>35.0%</td>
<td>10.4%</td>
<td>11.4%</td>
<td>43.2%</td>
</tr>
</tbody>
</table>
using a three-dimensional PDMS block to which other substrates are adhered by oxygen plasma treatment.

4. Conclusion

In this study, the deposition of a double layer on PDMS (TEOS-O₂/CH₄/PDMS) by AP-PECVD is proposed for surface modification of PDMS and for ensuring long-lasting hydrophilicity. The upper layer deposited using TEOS-O₂ is composed of hydrophilic SiOₓ particles, and the lower layer deposited using CH₄ is a highly cross-linked hydrocarbon layer. The hydrocarbon layer between the bare PDMS and the SiOₓ layer plays the role of a physical barrier that suppresses hydrophobic recovery to conserve the hydrophilicity of the SiOₓ layer. By a DOE study, the optimal processing conditions that yield PDMS with long-lasting hydrophilicity are identified. To analyze the long-lasting hydrophilicity of the deposited double layer (TEOS-O₂/CH₄/PDMS), the modified PDMS surfaces are characterized by static contact angle measurements, XPS analysis, and SEM images, and the results are compared with those for a single-layer PDMS sample without the PBL (TEOS-O₂/PDMS, obtained by AP-PECVD using TEOS-O₂ only). Surface morphology analysis of TEOS-O₂/CH₄/PDMS shows that the initial SiOₓ layer has been conserved over the aging time, while that of TEOS-O₂/PDMS without the PBL shows that the SiOₓ layer degrades steadily by the diffusion of PDMS oligomers, resulting in loss of hydrophilicity. The results of static contact angle observations on the modified surfaces correspond to those of the surface morphology analysis: the static contact angle of TEOS-O₂/CH₄/PDMS is nearly 0°, indicating high hydrophilicity. On the other hand, the static contact angle of TEOS-O₂/PDMS increases drastically from 0° to about 113° over the aging time. Therefore, it is believed that the surface modification with a double layer by AP-PECVD using TEOS-O₂ and CH₄ is a promising approach for applications where long-lasting hydrophilic surface property of inately hydrophilic materials is required.

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References


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