One-step microwave plasma enhanced chemical vapor deposition (MW-PECVD) for transparent superhydrophobic surface

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**Abstract.** We demonstrate a rapid and environmental friendly fabrication technique to produce optically clear superhydrophobic surfaces using poly (dimethylsiloxane) (PDMS) as a sole coating material. The inert PDMS chain is transformed into a 3-D irregular solid network through microwave plasma enhanced chemical vapor deposition (MW-PECVD) process. Thanks to high electron density in the microwave-activated plasma, coating can be done in just a single step with rapid deposition rate, typically much shorter than 10 s. Deposited layers show excellent superhydrophobic properties with water contact angles of ~170° and roll-off angles as small as ~3°. The plasma-deposited films can be ultrathin with thicknesses under 400 nm, greatly diminishing the optical loss. Moreover, with appropriate coating conditions, the coating layer can even enhance the transmission over the entire visible spectrum due to a partial anti-reflection effect.

**1. Introduction**

Fabrication of transparent superhydrophobic coating is attracting more and more attention owing to numbers of potential applications, such as high-performance solar cells, self-cleaning residential or vehicle glasses, as well as anti-contamination packaging. Essentially, superhydrophobic properties rely strictly on at least two key components: hydrophobic chemicals and a rough surface topology in micro-/nanoscale. Furthermore, it has been proved that effective and stable Cassie-Baxter non-wetting state requires multiscale roughness [1, 2]. However, increased irregularities generally lead to poor optical properties due to substantial light scattering [3]. Therefore, incorporation of transparent property into superhydrophobic coating requires optimized surface roughness in combination with ultrathin layers to minimize light scattering and bulk absorption, respectively [4, 5].

Several industrially viable techniques, for instance, spray coating [6], dip coating [7], or spin coating [8] of hydrophobic nanomaterials on substrates have been demonstrated for the fabrication of ultrathin wetting-resistant layers with low optical loss. Nevertheless, the aforementioned methods usually rely on multi-step and time-consuming processes necessary for nanoparticle synthesis or functionalization. Furthermore, they share common disadvantages on involving many reactive chemicals, especially volatile organic compound (VOC) that may pose health risks. Recently, chemical vapor deposition (CVD) assisted by radio frequency (RF) plasma has been employed to fabricate superhydrophobic coating via plasma polymerization [9]. The CVD process is even much faster when operated under...
MW plasma [10]. Although those plasma-based depositions are free from organic solvents the process still employs hazardous and flammable precursors. In an effort to develop an environmental friendly and fast method for generating transparent superhydrophobic layers, we investigated the feasibility of utilizing MW-PECVD with inert poly (dimethylsiloxane) (PDMS) liquid as the only input material used in the coating step. This organosiloxane compound is well known for its low hazard level, UV-resistance, and anti-corrosion abilities, ideal for use as a coating material [11]. Taking advantage of high electron density and collision frequency provided by MW-activated plasma [12], the PDMS molecules are expected to undergo substantial fragmentation into shorter reactive chains, which eventually polymerize again, thus forming a disordered 3-D structure on the surface. With this suitable surface roughness in combination with a minimum film thickness, superhydrophobicity and transparency can co-exist. Furthermore, the coating itself is a one-step process with a very fast deposition time of less than 10 s.

2. Experiment

2.1 Materials
Poly (dimethylsiloxane) or silicone oil, with a viscosity of 20 cSt was purchased from Sigma-Aldrich. This organosiloxane compound was chosen as a coating material since it contains inorganic backbone and hydrophobic methyl groups. Microscope glass slides (25.4 x 76.2 mm) were obtained from Sail Brand. Pure oxygen was supplied from Linde.

2.2. Plasma reaction system
A setup diagram of a custom-built system capable of performing plasma cleaning and ultrathin film coating via MW-PECVD technique is shown in Figure 1. A commercial microwave oven (800 W, 2.45 GHz) was employed as the plasma excitation source. A round quartz chamber (16 cm diameter and 5 cm height) with a gas inlet and outlet port was placed inside the microwave oven. Vacuum was generated by connecting the gas outlet to a mechanical pump (E2M8, Edwards) via a silicone tube passing through the microwave oven sidewall. Similarly, oxygen gas or vapor of coating precursors was delivered to the reaction chamber via another silicone tube connected to the inlet port. Oxygen flow rate was regulated using a flow meter, whereas the precursor rate is controlled through a heating temperature ranging from 50 °C to 130 °C. Plasma processing temperature in the chamber is typically 150-200 °C.

![Figure 1. Schematic diagram of a custom MW-PECVD system used in this study.](image)

2.3 Film deposition process
Microscope slides were used as planar substrates and were cleaned with oxygen plasma to remove surface contaminants at molecular level before the film deposition process. Briefly, glass samples were placed inside the chamber, which was then evacuated to a vacuum of ~0.1 mbar. Then oxygen gas was fed into until the chamber pressure reached ~0.3 mbar; pressure was maintained while
microwaves were applied to generate O₂ plasma for 15 s. The plasma cleaning process here also can activate radicals on the silica surface, which can form chemical bonds during the film deposition. After cleaning, the oxygen valve was closed and the vacuum in the chamber was restored to ~0.1 mbar. Meanwhile, liquid PDMS oil (4 ml) was heated at controlled temperatures to generate vapor, which is in thermal equilibrium with its liquid phase. Here, varied temperatures ranging from 50 °C to 130 °C were investigated for the impacts on film thickness and wetting properties. At the deposition process, microwaves were applied to activate air plasma in the vacuum chamber with the vapor fed through a needle valve. The plasma-aided chemical deposition was maintained for different periods of time, e.g. 5, 8, and 10 s.

2.4 Film characterizations

Static wetting properties of coating surfaces were evaluated through contact angles (CA) of distilled water using an optical contact angle measurement system (Dataphysics OCA-15EC). The contact angle measurement utilized probe liquids of droplet size ~2 μL placed at several locations on a sample surface. Dynamic wetting properties were determined via roll-off angle (RA) measurement of water droplet ~15 μL on a precise tilted platform. Surface topological structures and thickness of the deposited film were studied using scanning electron microscopy (SEM, FEI Quanta 400). The transmittance and reflectance spectra in visible region were recorded using a spectrometer (Blue-wave visible, StellarNet). The change of surface functional groups of the thin film was studied using Fourier transform infrared (FTIR) spectrometer (Bruker EQUINOX 55) operating in attenuated total reflectance (ATR) mode.

3. Results and discussion

![Figure 2](image)

**Figure 2.** Contact angle and roll-off angle measurements of thin films deposited via MW-PECVD with various PDMS heating temperatures (a). Here, all plasma processes were maintained for 5 s. The change of PDMS vapor pressure versus heating temperature is shown in (b).

The effect of the PDMS heating temperature upon resultant water-repellent properties are unveiled through CA and RA values as shown in Figure 2 (a). At low heating temperature regime, e.g. below 80 °C, the coated films show merely hydrophobic properties with contact angles residing in the range of 90-110°, which are similar to those obtained from smooth PDMS layers. Also water droplets stick on the surface without rolling. The absent evidence of roughness-amplified CA suggests that the deposited film is thin and smooth owing to low deposition rate caused by dilute PDMS molecules delivered into the reaction chamber. This is confirmed by the corresponding low vapor pressure at the same temperature range as shown in Figure 2 (b). Furthermore, increasing heating temperature beyond 80° C significantly improves film CA and reduces RA values, indicating that surface roughness starts to play a role and the Cassie-Baxter non-wetting state is predominant. Results show excellent water-repellent properties with a maximum CA of 169° and a minimum RA of 3°, achieved
with heating temperatures above 110°C. Albeit the ATM boiling point of the PDMS is greater than 140°C the vacuum environment helped to accelerate the vaporization rate and thus raises its vapor pressure.

![SEM micrographs](image)

**Figure 3.** SEM micrographs show cross sections of a CVD film (a), and MW-PECVD films with deposition time of 5 s (a), 8 s (b) and 10 s (c) respectively. Plane views of the MW-PECVD films with deposition time of 5 s, (e) and (f), show highly hierarchical roughness.

We decided to maintain the material heating temperature at 120°C and investigated the influences of plasma processing duration upon the films structural, wetting, and optical properties. As displayed in **Figure 3**, SEM images reveal cross sections of the MW-PECVD films deposited for 5 s, 8 s, and 10 s. Their corresponding thicknesses are 0.34±0.09 µm, 3.5±0.4 µm, and 6.9±0.2 µm, respectively, averaged from multiple samples. Results indicate rapid growth of film thickness with increasing deposition time, inferring a very quick coating mechanism. It also can be observed a highly porous and irregular surface morphology for all plasma-deposited cases, in comparison to a dense and smooth layer obtained from the CVD counterpart. Top views of the SEM images also confirm random fractal-like surface features, with roughness sizes mainly in submicron and nanoscale, which are highly favorable for wetting-resistant phenomena.

For the optical properties of the MW-PECVD films, light transmission and reflection in visible spectrum were determined for samples with different coating times with the results presented in Figure 4. The average transmission of a bare glass is ~ 89% with a hydrophilic surface CA of 34°. In contrast, all of the coated samples show excellent superhydrophobic properties with CA values near 170°. Overall, results are as expected, as increasing deposition time reduces the transmission due to more
absorption and scattering from films with thicker optical length. Of particular note is the sample with a deposition time of 5 s, where the transmission is even better than the bare glass sample. This is attributed to a couple of film properties. First, the thickness of the film is only 0.34±0.09 µm which greatly minimizes optical loss. Actually, this thickness result is consistent with previous work that suggests the optimized thickness for best coupling of transparent and superhydrophobic properties is below ~400 nm [4]. The other is the partial anti-reflection effect generated from the porous layer with nearly matched the refractive index [13]. Figure 4(b) show that the reflectance of all plasma-deposited films is lower than that of bare glass. In fact, thicker films show better anti-reflection behavior compared with thinner ones; however, their competing absorption and scattering grow faster. From results in Figure 4 it can deduced that the superhydrophobic coating with good optical transparent can be actually fabricated just within 5 s. This unrivaled coating time is made possible through a high electron density provided by the MW plasma.

![Figure 4. Transmission (a) and reflection (b) spectra of MW-PECVD films with different deposition times with their corresponding CA values included. The inset is a photograph showing water beads on a coated glass with high transparency.](image)

The influence of MW plasma on the films molecular structure was investigated through infrared absorption technique, with two major changes of functional groups observed for a MW-PECVD film in comparison with one deposited via conventional CVD, as shown in Figure 5. Firstly, the broadening of the band centered around 1,050 cm⁻¹ in the plasma-deposited case is suggesting an increasing degree of Si–O–Si network formation when compared to normal PDMS film, whose Si-O-Si characteristic spectrum generally consists of doublets at 1,085 cm⁻¹ and 1,020 cm⁻¹ [14, 15]. This particular spectrum broadening, as analogous to polyhedral oligomeric silsesquioxanes (POSS) structure, also indicates the existence of Si atoms, which bond to more than two O atoms that may involve in 2-D or 3-D crosslinks [16]. Another interesting point is the increase of the Si-O-Si/Si-CH₃ ratio for MW-PECVD films, which can be observed as the descent of the Si-CH₃ peaks at 780 cm⁻¹, 1,250 cm⁻¹, and 1,410 cm⁻¹, as well as Si-(CH₃)₂ and Si-(CH₃)₃ bands around 890-740 cm⁻¹. These FT-IR characteristics indicate a possible removal of methyl side groups due to the electron impact during the plasma process [17] followed by cross-linking and/or branching reactions forming complex network structures.
Figure 5. Comparison of FT-IR spectra of PDMS thin films deposited by (top) CVD technique and (bottom) MW-PECVD for 5 s.

The overall mechanism of the MW-PECVD process can be postulated based on information extracted from the abovementioned FT-IR results. As the reaction occurs in non-equilibrium MW plasma with high electron density and high power density, the vaporized PDMS substances are expected to suffer from molecular dissociation, excitation, and ionization caused by intense electron collision. The possible reaction schemes are proposed in Figure 6, where the electron impact results in PDMS chain scission producing smaller fragmented radicals. Also, the collision would create radicals at the polymer sidechain due to methyl abstraction process. This permits the formation branching or networked structures. Another competing chemical process taking place simultaneously is the plasma polymerization, which combines those dissociated radicals. Since the reactions are at relatively high energy and high entropy states, the subsequent structures are highly irregular with a high degree of roughness, favorable to superhydrophobic properties.
Figure 6. Possible chemical processes in MW plasma involving electron impact reactions, causing polymer chain fragmentation (a) and methyl abstraction (b). Those reactive components react and form more complex structures as shown in (c).

4. Conclusion
MW-PECVD technique has been demonstrated as efficient and environmental-friendly technique to produce transparent superhydrophobic surface within single coating step (excluding sample cleaning). PDMS liquid, used as a coating material, was vaporized and delivered into a MW-plasma chamber allowing electron impact processes to decompose the polymer chains into fragmented radicals. These highly reactive chemical species recombined via plasma polymerization, thus forming a disorder solid networked structure deposited on a glass substrate. The threshold of precursor vapor pressure to achieve multiscale roughness coating is above 0.25 mbar, which results in superhydrophobic properties. Furthermore, plasma processing time has shown a strong influence on film thickness and subsequent wetting and optical properties. With optimized plasma deposition time of merely 5 s, a superhydrophobic layer (CA ~170°, RA ~3°) with a thickness of ~340 nm can be fabricated. This ultrathin coating layer causes virtually no optical loss as the film also possesses anti-reflection properties which permit more light to pass through.

5. References
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