

Development of Durable Nanostructured Superhydrophobic Self-Cleaning Surfaces on Glass Substrates

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ABSTRACT

High quality SiO₂ based transparent superhydrophobic coatings with double-roughness microstructure and high durability were deposited onto glass substrates by the Combustion Chemical Vapor Deposition (CCVD) technique and the combination of an innovative device and the CCVD. A contact angle of higher than 165°, a rolling angle of <5°, a haze of <0.5%, and an increased transmittance by 2% higher than bare glass have been achieved by the CCVD technique. By the combination of the innovative device and the CCVD, a contact angle of 137° has been achieved after being wiped by a standard automobile wiper for 60,000 times with coating's morphology keeping the same.

Keywords: nanostructure, superhydrophobic, durable, coating, CCVD

1 INTRODUCTION

Studies of superhydrophobic self-cleaning surfaces have been attracting increasing interest in recent years for both fundamental research and practical applications. The applications of superhydrophobic self-cleaning surfaces include architectural glass, automotive glass, solar panels, shower doors, and nanochips, etc. [1-3]. Wide usage of self-cleaning surfaces will result in huge energy savings by removing the need for washing, scrubbing, and chemical polishing of windows, ceramics, and other surfaces. In addition to a reduction in cleaning requirements, these superhydrophobic surfaces have additional benefits, such as improved safety when driving in severe rain and snow, and improved efficiency in solar cells.

The development of superhydrophobic self-cleaning surfaces was first inspired by the observation of natural cleanness of lotus leaves [4] and other plant leaves [5]. The typical superhydrophobic self-cleaning effect in nature is found from lotus leaves. Scanning electron microscopy (SEM) studies on lotus leaves [5,6] revealed that a microscopically rough surface consisting of an array of randomly distributed micropapillae with diameters ranging from 5 to 10 μm. These micropapillae are covered with waxy hierarchical structures in the form of branch-like nanostructures with an average diameter of about 125 nm. Motivated by the lotus leaf, many techniques have been

being developed to create nanostructures mimicking the lotus effect from many organic and inorganic materials [7,8]. However, existing hydrophobic coatings either have low transmittance not suitable for windows and solar panels or not as hydrophobic as lotus leaves or low durability.

In this work, an open atmosphere CCVD technique and the combination of an innovative device and CCVD were employed to deposit SiO₂ based superhydrophobic coatings onto glass substrates. The coatings' morphological, hydrophobic, and other physical properties are presented.

2 EXPERIMENTAL PRECEDURES

2.1 Superhydrophobic coatings by the CCVD Process

In the CCVD process, shown in Figure 1 [9], precursors are dissolved in a solvent, acting also as the combustible fuel. This solution is atomized to form submicron droplets by the proprietary Nanomiser™ device. The resulting vaporous fog is then convected by an oxygen containing stream to a flame. The heat from the flame provides the energy required to flash vaporize the ultrafine droplets and for the precursors to react and vapor deposit on the substrates. The CCVD technique uses a wide range of inexpensive, soluble precursors that do not need to have a high vapor pressure. The key advantages of the CCVD technique include:

- Open-atmosphere processing
- High quality at low cost
- Wide choice of substrates and
- Continuous production capability

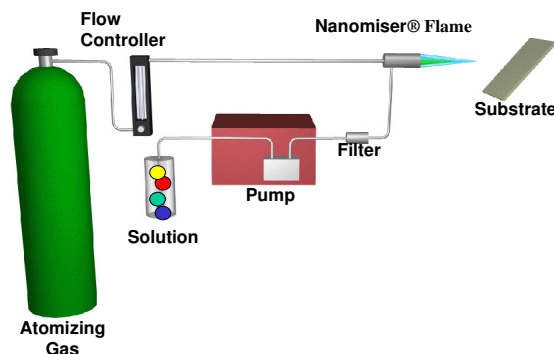


Figure 1. Schematic representation of the CCVD system

In this work, the coatings were fabricated by either the CCVD technique or a combination of an innovative device and CCVD. Prior to depositions, the glass substrates were ultrasonically cleaned in organic solvents such as isopropanol, rinsed in deionized water, and blown dry using nitrogen. The substrate was then mounted on a metal chunk or the top of a back heater. Key process parameters include deposition temperature, glass surface temperature, and coating composition.

2.2 Analytical techniques

Equilibrium, receding, and advancing CAs were measured by a CA measuring system (G10, Kruss USA). Equilibrium CAs were measured using deionized water droplets of approximately 1 – 2 mm in diameter. If not indicated specifically, all the CAs in the following sessions are equilibrium water CAs. Three data points were tested on all samples.

The coating's morphology was observed by SEM (Hitachi s-800 and s-4800). Transmittance and reflectance in the visible range were measured by a spectrometer (PERKIN-ELMER Lambda 900 UV/VIS/NIR spectrometer). Surface roughness (as root mean square, RMS) was evaluated by an optical profilometer (Burleigh Instruments, Inc.). Haze in the visible range was characterized by a haze meter (BYK Gardner Haze Meter). Coating's durability was tested by measuring the CA before and after wiping the coating by a standard automobile wipe for certain times.

3 RESULTS AND DISCUSSION

Superhydrophobic coatings have been grown by many techniques such as CVD [7] and sol-gel [8]. These techniques can require costly starting materials, and/or are time consuming and have low throughput. The open atmosphere CCVD and its combination with an innovative device offer an attractive alternative to grow durable transparent superhydrophobic coatings on glass and plastic substrates with good yield and high throughput potential. SiO₂ is chosen as primary coating material because of its low cost, ease to make, and refractive index match between the coating and the substrate, which reduces reflectivity of the coated specimens.

To achieve low haze and high transmittance, the feature size of the coating must be much smaller than the visible wavelength to reduce large light scattering. Figure 2 shows the SEM image of a typical SiO₂ coating on glass substrate by the CCVD technique. The coating has a rough surface and double surface roughness, in which coarse features are composed of nanostructures of 30 to 200 nm. The double roughness morphology is similar to the topology of lotus leaves but smaller. The nanometer sized hierarchical structure is essential to simultaneously achieve low haze, increased transparency, and superhydrophobicity.

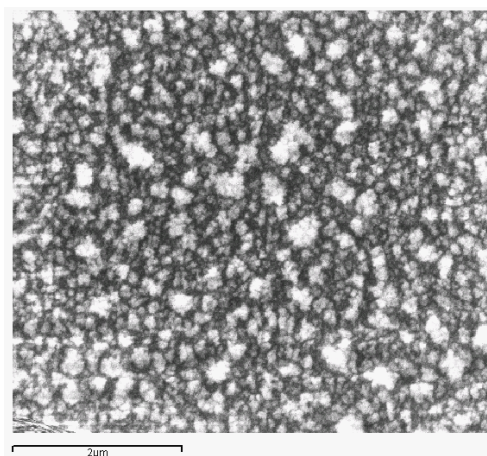


Figure 2. SEM image of a typical CCVD SiO₂ based superhydrophobic coating on glass substrate

A CA of over 165° was achieved on as-deposited samples with a rolling angle of less than 5°. The haze of the samples is less than 0.5%. For reference, the bare glass substrate treated with the same fluorinate silane has a CA of approximately 110° with a haze of about 0.2%. The transmittance and reflectance of bare glass are in the range of 91.8 to 92.6% and 7.4 to 8.5%, respectively while those of the CCVD SiO₂ coated samples are in the range of 93.9 to 94.5% and 5.6 to 6.2%, respectively. The SiO₂ coated glass is hyper-transparent with an increased transmission of about 2% higher and a reduced reflectance of about 2% lower than bare glass substrate, suggesting the CCVD SiO₂ coatings reduce reflection in the visible range and are of anti-reflection, which will benefit many applications, especially solar cells, lighting and imaging.

In addition to CA, durability is another important factor for many practical applications of self-cleaning surfaces. Durability tests were conducted by moving the samples across a defined distance on a polishing cloth surface. Force was determined by the weight of the samples themselves. CA was measured after each two passes across the abrasion surface. In total, twenty passes were completed for each sample. In a previous report [10], coating's durability was improved considerably by a post-deposition treatment process. In this report, coatings' composition was studied to improve their durability. Figure 3 shows the contact angle of samples with different compositions as a function of abrasion pass. For the sample with composition A, its initial contact angle was 170°. It decreased rapidly in the first 10 passes of abrasion. After 20 passes the contact angle decreased to 150°. It was noticed that after the abrasion test, the rolling angle increased significantly. For the sample with composition B, its initial contact angle was 170°. After 20 passes of abrasion it decreased to 160°, which is even higher than the sample with a post-deposition treatment [10]. Therefore, in addition to processing conditions and post-deposition treatment, coating's composition plays a critical role in its hydrophobicity and durability. Figure 4 shows the SEM

image of a superhydrophobic coating after the abrasion test. It can be seen that the coating's surface became much smoother and lost its double roughness, which leads to decreased contact angle and increased rolling angle. These results suggest that initial superhydrophobic surfaces are not strong enough to keep their superhydrophobicity to meet a number of practical applications.

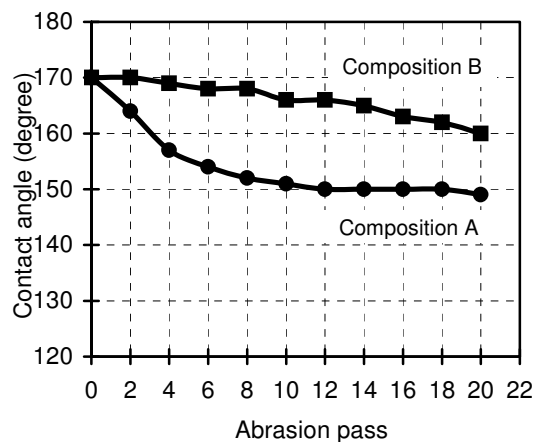


Figure 3. Contact angle of SiO₂ based coatings as a function of abrasion pass with different compositions

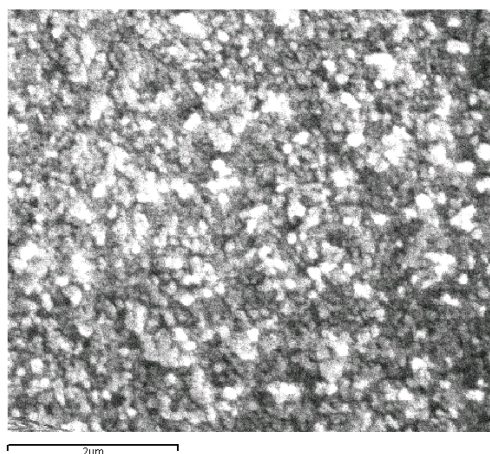


Figure 4. SEM image of a superhydrophobic coating after 20 passes of abrasion test

To further improve durability for practical applications, *n*Gimat and its commercialization partner Honda R&D designed and manufactured an innovative device (WRIN). This WRIN device and related process embed ultrafine particles into the substrate surface and forms robust structures. Figure 5 shows plan view and cross sectional SEM images of a hydrophobic coating by the WRIN device. It can be seen that larger dual-sized semi-spherical and irregular features with a size from 0.2 to 1.5 µm were embedded into the glass surface. Smaller features with size 200 nm or less were distributed between the larger features. The cross sectional SEM image (Figure 5 (b)) clearly shows an embedded particle which deformed the glass surface. A defused interface layer was formed between the embedded

particle and the glass substrate. Energy dispersive X-ray (EDX) spectra were collected from point 1 and point 2 in Figure 5 (b). The EDX spectra clearly show a distinct intermediate layer between the embedded particle and the glass substrate, which provide strong bonding and therefore, improved abrasion resistance.

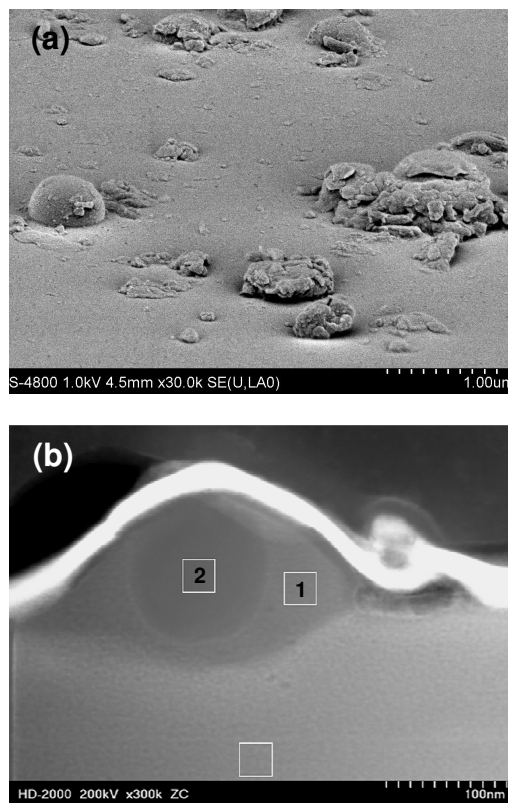


Figure 5. (a) Plan view (75° tilt) and (b) cross sectional SEM images of a sample deposited by the WRIN device. EDX spectra collected from (b) point 1 and (b) point 2 showed a change in composition.

To further increase the distribution density of the deposited pillars and hence, coating's hydrophobicity, after the larger pillars were deposited by the WRIN device, smaller features with a size of 50 nm or less were deposited by the CCVD technique. These smaller features cover both the larger pillars and the valleys between the larger pillars to form double-roughness structure. The samples deposited by the combination of the WRIN device and the CCVD technique were subjected to abrasion tests by a standard automobile wiper. After being wiped for 60,000 times and re-treated, the contact angle of the sample decreased from 151° to 137°. The morphology of the sample after abrasion tests is shown in Figure 6. The smaller features by the CCVD process on the larger pillars by the WRIN device were wiped off. The larger pillars and the smaller features in the valleys between the larger pillars are kept almost the same before abrasion tests, showing the high robustness of the larger pillars and their protection to the smaller features with less robustness. The overall durability of the double-

sized super-hydrophobic structure has been improved significantly. More optimization and tests will be conducted to optimize both the durability and hydrophobicity that will ultimately meeting the practical requirements.

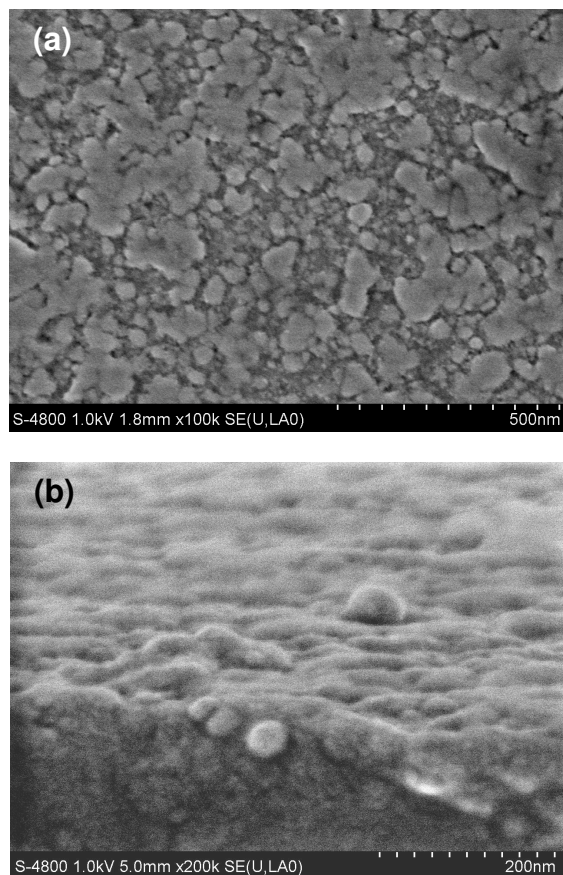


Figure 6. SEM images of a sample deposited by the combination of the WRIN device and CCVD technique, (a) no tilt and (b) tilt 75°

4 SUMMARY

As a summary, transparent superhydrophobic surfaces with high performance have been successfully prepared on glass substrates by the CCVD technique and the combination of the WRIN device and the CCVD technique. A contact angle of higher than 165°, a rolling angle of <5°, a haze of <0.5%, and an increased transmittance by 2% higher than bare glass have been achieved by the CCVD technique. By the combination of the innovative device and the CCVD, a contact angle of 137° has been achieved after abrasion tests by a standard automobile wiper for 60,000 times with coating's morphology keeping the same.

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