Hypertransparent Nanostructured Superhydrophobic Self-Cleaning Coatings on Glass Substrates

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ABSTRACT

In this paper, high quality SiO_2 based hypertransparent superhydrophobic coatings with double-roughness microstructure were successfully deposited onto glass substrates by the Combustion Chemical Vapor Deposition (CCVD) technique. A contact angle of higher than 165°, a rolling angle of $<5^o$, a haze of $<0.5\%$, and an increased transmittance by 2% higher and a reflectance of 2 % lower than bare glass have been achieved.

Keywords: nanostructure, superhydrophobic, self-cleaning, coating, CCVD

1 INTRODUCTION

Studies of superhydrophobic self-cleaning surfaces have been attracting increasing interest in recent years as a result of numerous new prospects for both fundamental research and practical applications. The applications of self-cleaning surfaces include architectural glass for homes and commercial buildings, automotive glass, shower doors, solar panel glass covers, nanochips, and microfluidic systems [1-3]. With wide usage of self-cleaning surfaces, over $100 million a year in energy savings will be generated as a result of 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 (anti-reflective and self-cleaning properties).

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, which is revered as a symbol of purity for its ability to maintain clean leaves even in heavily contaminated waters. In studies of lotus leaves by scanning electron microcopy (SEM) [5,6], it was revealed that the key features of the lotus leaf are 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 nature and the superhydrophobic self-cleaning performance of the lotus leaf, many techniques have been being developed to create nanostructures mimicking the lotus effect from many materials, both in organic and inorganic [7,8]. However, existing hydrophobic coatings either have low transmittance which is not suitable for windows and solar panels or not as hydrophobic as lotus leaves.

In this work, an open atmosphere CCVD technique was employed to deposited SiO_2 based superhydrophobic coatings onto glass substrates that actually increase light transmission and are thus hypertransparent. 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 [9], as shown in Figure 1, precursors, which are the metal-bearing chemicals used to coat an object, are dissolved in a solvent, which typically also acts as the combustible fuel. This solution is atomized to form submicron droplets by means of the proprietary Nanomiser™ device. These droplets are then convected by an oxygen containing stream to the flame where they are combusted. A substrate (the material to be coated) is coated by simply drawing it over the flame plasma. The heat from the flame provides the energy required to evaporate the ultrafine droplets and for the precursors to react and to 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
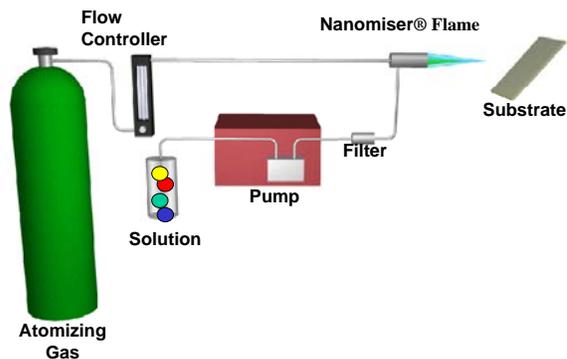
Figure 1. Schematic representation of the CCVD system

In this work, all the coatings were fabricated by the CCVD technique addressed previously. 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, solution concentration, motion speed, coating thickness, and coating composition.

2.2 Analytical techniques

To measure water contact angle (CA), the coated specimens were surface treated with a fluorinated silane by immersing the specimens in a hexane solution of the fluorinated silane (with a volume ratio of silane to hexane of 1:50) for 10 min. The specimens were then rinsed by hexane and deionized water and blown dry by nitrogen gas. 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. To measure advancing CA, a water droplet of about 1 – 2 mm in diameter was first placed on the film surface. The cursor line was placed in front of the water droplet. The droplet was then enlarged by pushing more water through the needle. While the droplet volume increases, the contact line between water and the solid surface moved forward. The advancing CA was measured once the droplet front reached the cursor line. To measure receding CA, a large water droplet of about 5 mm in diameter was placed on the solid surface first. The cursor line was placed between the syringe needle and the droplet front. The droplet volume was decreased by sucking water back into the syringe. When the contact line began moving and the droplet front reached the cursor line, the receding CA was recorded. During the measurements of advancing and receding CAs, the syringe needle was always in the water droplet. Three data points were tested on all samples.

The coating's morphology was observed by SEM (Hitachi s-800). 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).

3 RESULTS AND DISCUSSION

Superhydrophobic coatings have been grown by many techniques such as CVD [7] and sol-gel [8]. These techniques require costly starting materials, and/or are time consuming and have low throughput. The low cost CCVD technology offers an attractive alternative to grow nanostructured superhydrophobic coatings on glass and plastic substrates with good yield and high throughput potential. SiO_2 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 SiO_2 coating on glass. 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 leaf. The nanometer sized hierarchical structure is essential to simultaneously achieve low haze, increased transparency, and superhydrophobicity.
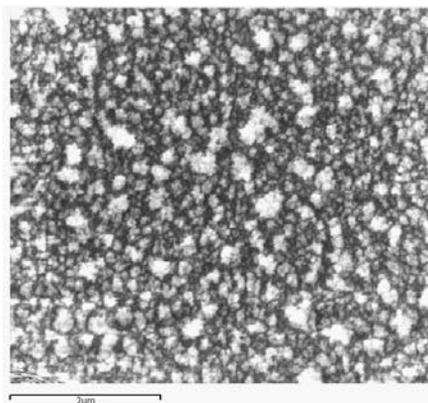
Figure 2. SEM image of a typical CCVD SiO_2 based superhydrophobic coating on glass substrate

The relationship between CA and surface roughness of the SiO_2 coatings is present in Figure 3. It is clear that CA increases rapidly with the increase of surface roughness up to about 1.5 nm. When surface roughness reaches 1.5 nm or higher, CA remains almost constant. A CA of over 165° was achieved with surface roughness ranging from 1 to 20 nm. For reference, the bare glass substrate coated with the same fluorinate silane has a CA of approximately 110° with a surface roughness of about 0.70 nm. For comparison, photographs of water droplets sitting on bare and silane/SiO_2-CCVD coated glass are shown in Figure 4. Water droplets spread out on bare glass with a CA of less than 20°, showing the nature of hydrophilicity of glass (Figure 4 (a)). After coated with the nanostructured SiO_2 film and surface treated with the fluorinated silane, water droplets bead up to form spheres, showing superhydrophobicity (Figure 4 (b)).

Haze of the superhydrophobic coatings is another important property for many applications. Haze of the bare glass is about 0.2%. As shown in Figure 5, when surface roughness is less than 2.0 nm haze increases slightly with increasing roughness. Beyond a roughness of 3 nm haze increases almost exponentially with increasing roughness. For samples with surface roughness less than 2.0 nm, a

haze of less than 0.5% was obtained with a contact angle of over 165° and a CA hysteresis of less than 5°.
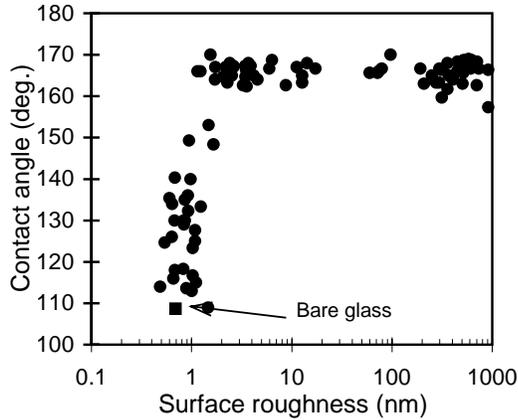
Figure 3. Contact angle of the SiO_2 based coatings as a function of surface roughness
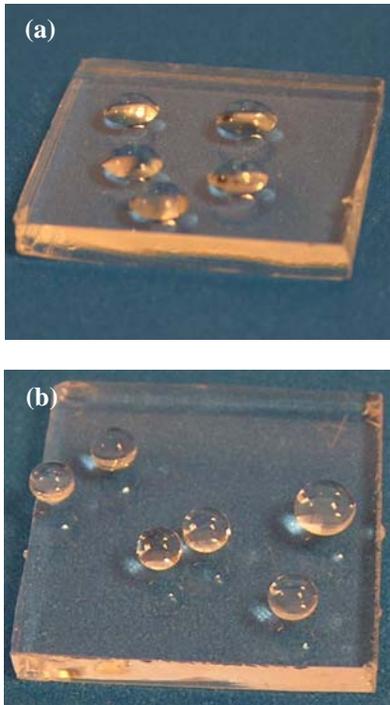
Figure 4. Optical images of water droplets sitting on (a) bare glass substrate and (b) fluorinated silane coated CCVD SiO_2 coating on glass substrate

Figure 6 shows typical transmittance and reflectance spectra of one side CCVD SiO_2 coated and bare glass substrates in the visible range. 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 the CCVD SiO_2 coated samples are in the range of 93.9 to 94.5% and 5.6 to 6.2, respectively. The SiO_2 coated glass is hypertransparent since it has increase transmission by about 2% higher. Reflectance is about 2% lower than bare glass substrate, suggesting the CCVD SiO_2 coatings reduce reflection in the visible range and are of anti-reflection, which will benefit

many applications, especially solar cells, lighting and imaging. For imaging applications the *n*Vision™ coating line is being launched based on the properties of these coatings.
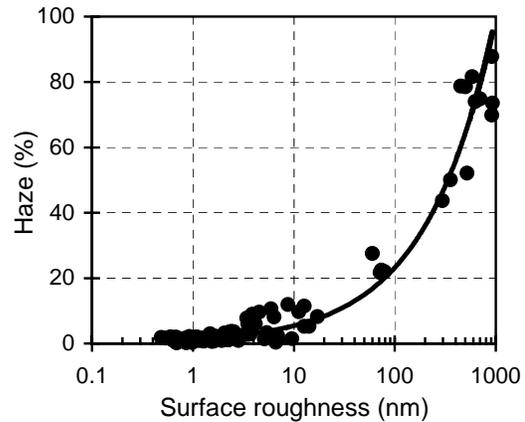
Figure 5. Haze of the SiO_2 based coatings as a function of surface roughness
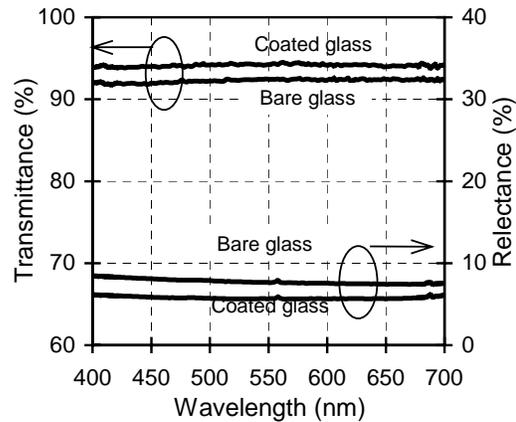
Figure 6. Transmittance and reflectance of a typical SiO_2 based superhydrophobic coating on glass

In this work, process parameters such as deposition temperature, deposition time/lap, and flame motion speed were investigated to optimize the hydrophobicity. Figure 7 shows the CA and CA hysteresis of SiO_2 coatings deposited at a certain solution concentration and different processing conditions as a function of motion speed. As shown in Figure 7 (a), all other samples maintain almost the same CAs with the increase of motion speed. CA hysteresis, which is directly related to rolling angle, is another important factor to evaluate superhydrophobic self-cleaning surfaces. The smaller the CA hysteresis is, the easier the water droplets roll off the surface, namely the higher the self-cleaning performance. Figure 7 (b) shows the effects of motion speed on CA hysteresis as a function of deposition variables including one or two laps. All samples but one show nominal change in angle hysteresis with the increase of motion speed.
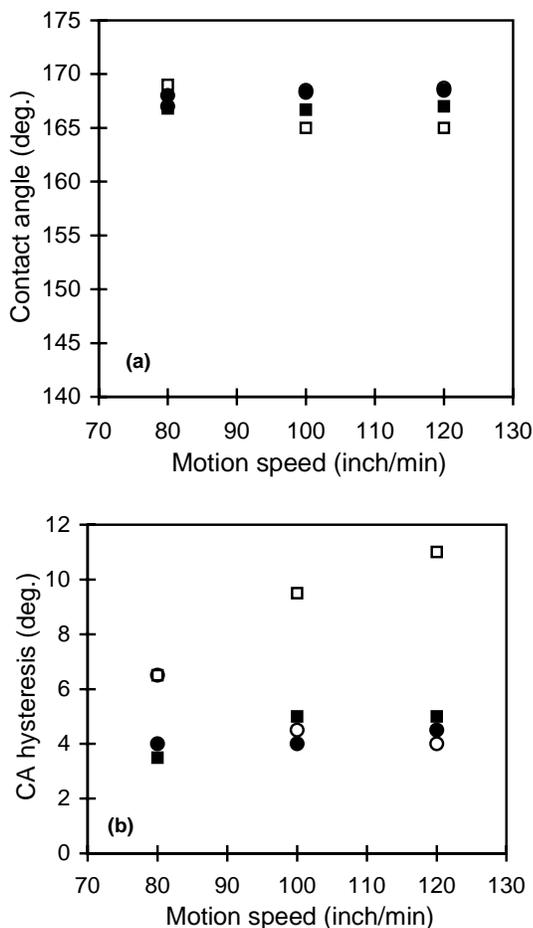
Figure 7. (a) CA and (b) CA hysteresis of CCVD SiO$_2$ coatings deposited at different processing conditions as a function of processing motion speed. Each symbol represents a change in processing condition.

Abrasion resistance is an important factor for many practical applications of self-cleaning surfaces. Abrasion tests were conducted at *n*Gimat 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. Figure 8 shows abrasion test results of two differently processed CCVD SiO$_2$ coatings. The initial CA of the A-processed coating was 170°. It decreased rapidly in the first ten passes of abrasion. After ten passes the contact angle remained almost constant at 150°. It was noticed that after the abrasion test, the rolling angle increased significantly. To increase the strength of the superhydrophobic surfaces, a sample was differently B-processed then coated with silane. As shown in Figure 8, its initial CA was 168°, about 2° lower than that of the A-processed one. In the first 4 passes, the CA decreased rapidly to 159°. After 4 passes, the CA decreased minimally. After 20 passes the final CA was 157°, which is

8° higher than that of the A-deposited sample, suggesting the B-processing increased the coating's strength.
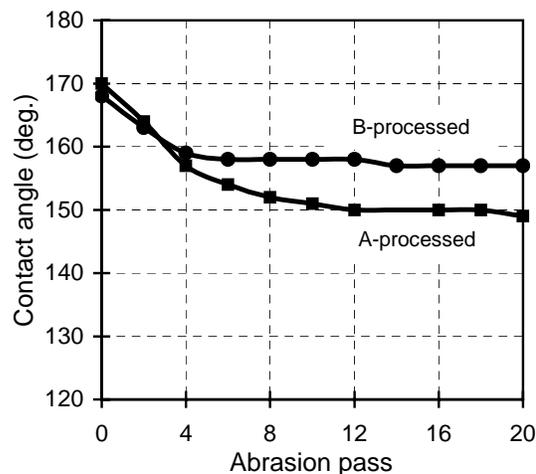
Figure 8. Contact angle as a function of abrasion pass of A and B processed CCVD coatings on glass

4 SUMMARY

As a summary, hypertransparent superhydrophobic surfaces with high performance have been successfully prepared on glass substrates by the CCVD technique. A contact angle of 170°, a rolling angle of <5°, a haze of <0.5%, and a transmittance 2% higher and a reflectance of 2 % lower than bare glass have been achieved.

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