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Ceramics International 38 (2012) 2971–2976
CERAMICS INTERNATIONAL
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Non-fluorinated, room temperature curable hydrophobic coatings by sol–gel process

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Received 21 October 2011; received in revised form 28 November 2011; accepted 28 November 2011
Available online 6 December 2011

Abstract

Non-fluorinated hydrophobic silica surfaces were generated on soda lime glass (SLG) substrates using hexamethyldisilazane (HMDS) as a surface modifying agent. Silica coatings were fabricated by dip coating of a sol derived from base catalyzed hydrolysis and condensation of tetraethoxysilane (TEOS). Two methodologies were adopted to generate the hydrophobic surface; one where the hydrophilic silica coated surface was treated by immersion into different concentrations of alcoholic solutions of HMDS varying from 2.5 wt% to 15 wt%. In the other method, HMDS was directly added to a mixture of TEOS, water, ethanol, and ammonium hydroxide and coatings were deposited using this sol by dip coating and spray coating. Water contact angles (WCA) were measured to study the effect of HMDS treatment times and concentrations on hydrophobicity in the first case, and in the second case, WCA were measured for dip and spray coated samples. UV–visible transmission, scratch resistance, and thermal stability of the coatings were determined. The WCA increased from 66 ± 2° to 125 ± 4° after the treatment of the silica coatings with HMDS. In case of coatings generated from direct addition of HMDS to silica sol, WCA varied from 145 ± 2° to 166 ± 4° for dip and spray coated surfaces respectively. Surface morphology was studied to explain the difference in hydrophobicity of coatings generated using the two methods.

Keywords: A. Sol–gel processes; A. Films; B. Surface; C. Optical properties; E. Functional applications

1. Introduction

Hydrophobicity is a property that provides water repellency and non-wettability of a solid surface. The fabrication of hydrophobic coatings is an active area of research in recent years because of its wide range of applications. Sol–gel process has been widely used in the research area of superhydrophobicity due to its unique advantages such as low temperature processing, easy functionalization of surfaces and high homogeneity of final products. Chemical modification of smooth surfaces can lead to a hydrophobic surface with water contact angles up to ~130° [1–4]. Fluorosilanes [1–3], polyvinylidene fluoride [4] are used in small amounts along with organically modified silanes to synthesize low surface free energy sols for chemical modification of any surface. However, fluorinated materials are not eco-friendly and hence, other surface modifying materials like silylating agents are being investigated as alternatives for generating hydrophobic coatings.

A silica surface can be made hydrophobic by chemical reaction (referred to as functionalizing, grafting, or silylating) with certain coupling agents to form trimethylsilyl (TMS, $-Si(CH_3)_3$) surfaces. Rao et al. [5] studied the silylation using dimethylchlorosilane (DMCS) on silica coatings derived from methyltrimethoxysilane (MTMS). They reported that the hydrophobicity increased with increase in concentration of DMCS. Mahadik et al. [6] studied the effect of using trimethylchlorosilane (TMCS) as silylating agent on the silica coatings prepared from methyltriethoxysilane (MTES) and trimethylmethoxysilane (TMMS). They reported that the hydrophobicity increased with increase in treatment (silylation) time [6]. Latthe et al. [7] reported on silylation of silica sols derived from tetraethoxysilane (TEOS) and vinyltrimethox-

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doi:10.1016/j.ceramint.2011.11.075

ysilane (VTMS). They showed that when molar ratio (M) of VTMS/TEOS was varied, surface structure and hydrophobicity also changed [7]. TMS functionalization of silica surfaces can also be done by a different method by reaction of silica sol with silylating agent like hexamethyldisilazane (HMDS) or chlorotrimethylsilane in the vapor phase [8–13]. Suratwala et al. [14] however used a different approach to generate hydrophobic coatings. Silica sols synthesized by Stöber process were treated with silylating agent HMDS to produce TMS functionalized colloids. HMDS was reacted with these silica sols in suspension to produce highly hydrophobic, TMS functionalized sols. They reported that the variation in starting surface species, the HMDS reaction time, and concentration strongly affect the amount of TMS coverage that takes place [14]. Bhagat et al. [15] also used HMDS as silylating agent and prepared a sol by changing the molar ratio of tetramethoxysilane (TMOS)/methanol and adding the HMDS to the sol to achieve hydrophobicity. Li et al. [16] have reported that super-hydrophobic nanosilica can be prepared by surface modification using HMDS.

In most of the investigations where silylating agents were used to modify silica coatings, the coatings were derived from tetramethoxysilane (TMOS) precursor. Since TEOS as a precursor is more suitable for large scale production of silica coatings when compared to TMOS (which yields methanol on hydrolysis and alcohol condensation), silica sol using TEOS was synthesized in the present study. Moreover all the previous reports on the silylation of surfaces mention the use of toxic hexane and decane as solvents to make HMDS solutions. In the present study, isopropyl alcohol (IPA) was used along with HMDS which has not been reported so far. Two methods were adopted to generate the hydrophobic surface; one by treating the hydrophilic silica coating with HMDS as silylating agent and the other by addition of HMDS to silica sol which was coated on the substrate. The coatings were assessed for their hydrophobicities and UV–visible light transmission.

2. Experimental

2.1. Materials

The silica sols in the present study were prepared by the conventional sol–gel process using the following chemicals: tetraethoxysilane (TEOS, ABCR GmbH and co.), hexamethyldisilazane (HMDS, Sigma–Aldrich® Chemie GmbH), ethanol (EtOH), isopropyl alcohol (IPA) (Qualigens Fine Chemicals), and ammonium hydroxide (NH_4OH, Assay – 25 wt%, Finar Chemicals (India) Pvt. Ltd.).

Soda lime glass with a nominal composition of the major metallic elements as Na = 15.5 wt%, Mg = 4.2 wt%, Si = 63.3 wt%, Ca = 14.3 wt%, Al = 1.4 wt% was used as the substrate.

2.2. Sol synthesis and deposition of thin films

Two methods were adoped to prepare the hydrophobic films

(a) Silica films treated with silylating agent

The silica sol was synthesized using the following chemicals TEOS:EtOH:H_2O:NH_4OH in the molar ratio of 1:36.4:6.6:0.25 and NH_4OH (6 M) used as a catalyst. The mixture was allowed to stir for 24 h at 25 °C and the cleaned glass substrates were dipped vertically into the sol for 1 min and withdrawn at a speed of 5 mm/s. The films were dried at 25 °C and annealed at 300 °C for 1 h followed by room temperature treatment in alcoholic HMDS solution with the concentrations varying from 2.5 wt% to 15 wt% HMDS in IPA. All the films were prepared at room temperature and the treatment time was varied from 1 h to 3 h. The surface treated silica films were annealed at 150 °C for 1 h in air using a drying oven.

(b) Silylating agent added to silica sol

The sol was prepared by mixing TEOS:EtOH:HMDS:H_2O:NH_4OH in the molar ratio of 1:36.4:1:6.6:0.25 respectively. HMDS was added to the silica sol and stirred for 24 h. The SLG substrates were dipped vertically in the sol for 1 min and withdrawn at a speed of 5 mm/s. Manual spray coating was also carried out. Both the dip coated and spray coated films were dried at an ambient temperature of 25 °C and annealed at 150 °C in air using a drying oven.

2.3. Characterization

Hydrophobicities of the coatings as well as the wettabilities of substrates prior to coating were measured using a Drop Shape Analyser (DSA) (Krüss GmbH Germany). Contact angles were measured by fitting a mathematical expression to the shape of the water drop, and then calculating the slope of the tangent to the drop at the liquid–solid–vapor interface line. The volume of water droplet was ~4 μl and at least ten measurements were taken. Average of these values was reported as water contact angle (WCA) on the substrate. In case of surface treatment of silica films with HMDS, contact angles were measured before and after treating with HMDS. The surface morphology of the silica coated thin films was studied by using Scanning Electron Microscope (SEM) (Hitachi S3400 N). Transmittance of the coatings was measured by Varian Cary 5000 UV-Vis-NIR Spectrophotometer. Thickness of the transparent coatings measured using Filmetrics Inc. F20 equipment. Hardness of the coatings was evaluated by Pencil scratch tester (Sheen Instruments Ltd. Wolff Wilborn pencil tester GEF 720N) according to ASTM D 3363-05.

3. Results and discussion

3.1. Reaction mechanism

The proposed reaction mechanism for the coatings generated using the two methods are given below:

(a) Silica films treated with silylating agent

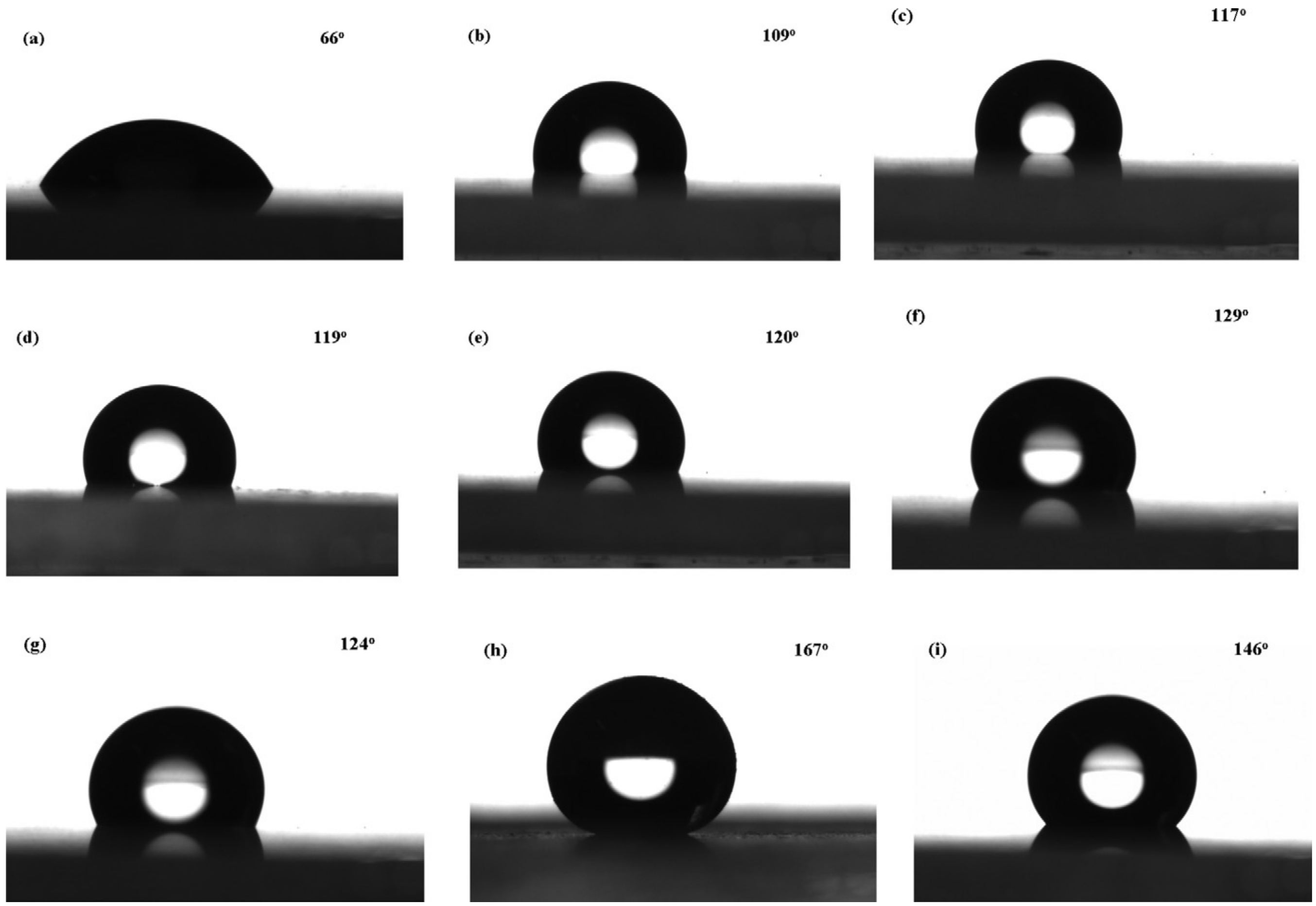


Fig. 1. Water drop images of (a) 0 wt%; (b) 2.5 wt%; (c) 5 wt%; (d) 7.5 wt%; (e) 10 wt%; (f) 12.5 wt%; (g) 15 wt% HMDS treated silica coatings for 3 h (h) spray coated and (i) dip coated HMDS + silica sol.

Hydrolysis:

$$\mathrm{Si(OCH_2CH_3)_4 + 4H_2O \rightarrow Si(OH)_4 + 4CH_3CH_2OH} \qquad (1)$$

Condensation:

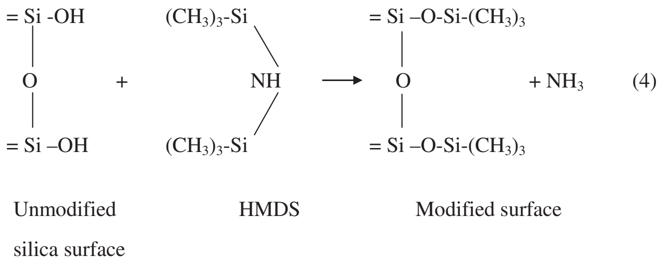
Water condensation:

$$n\mathrm{Si(OH)_4} \rightarrow n\mathrm{SiO_2} + 2n\mathrm{H_2O} \qquad (2)$$

Alcohol condensation:

$$n\mathrm{Si(OH)_4} + n\mathrm{Si(OCH_2CH_3)_4} \rightarrow 2n\mathrm{SiO_2} + 4\mathrm{nCH_3CH_2OH} \qquad (3)$$

The sol when deposited on a SLG substrate forms a hydrophilic silica film, due to the presence of –Si–OH groups on the surface as shown in schematic below:



$$\begin{array}{ccccc} =\mathrm{Si\text{-}OH} & & \mathrm{(CH_3)_3\text{-}Si} & & =\mathrm{Si\text{–}O\text{-}Si\text{-}(CH_3)_3} \\ | & & \diagdown & & | \\ \mathrm{O} & + & \mathrm{NH} & \longrightarrow & \mathrm{O} \quad + \mathrm{NH_3} \quad (4) \\ | & & \diagup & & | \\ =\mathrm{Si\text{–}OH} & & \mathrm{(CH_3)_3\text{-}Si} & & =\mathrm{Si\text{–}O\text{-}Si\text{-}(CH_3)_3} \end{array} \qquad (4)$$

Unmodified silica surface HMDS Modified surface

The surface modification of the coated thin films on substrate from hydrophilic to hydrophobic takes place on treatment with HMDS. In the surface modification, the hydrolytically stable –Si–$(CH_3)_3$ groups reacts with the hydroxyl groups on the silica surface that generates hydrophobicity.

(b) Silylating agent added to TEOS, H_2O, C_2H_5OH, NH_4OH mixture

Here, initially hydrolysis of TEOS takes place and condensation of silanol groups takes place with HMDS, to form a three-dimensional silica network when deposited on the surface of the substrate.

Hydrolysis:

$$\mathrm{Si(OC_2H_5)_4 + H_2O \rightarrow Si(OH)(OC_2H_5)_3 + C_2H_5OH} \qquad (5)$$

Condensation:

$$\mathrm{2Si(OH) + (CH_3)_3{-}Si{-}NH{-}Si{-}(CH_3)_3 \rightarrow 2Si{-}(O{-}Si{-}(CH_3)_3)_2 + NH_3} \qquad (6)$$

Addition of HMDS catalyzes the formation of silica nanoparticles. The HMDS reacts with –Si–OH groups of silica particles formed in situ and generates the superhydrophobicity through the attachment of –O–Si–$(CH_3)_3$ groups on the surface of the silica particles in the sol.

3.2. Effect of HMDS concentration and treatment time on hydrophobicity

The surface chemical modification of the silica films was done by varying the concentration of the silylating agent HMDS in IPA from 2.5 wt% to 15 wt%. The treatment times were also varied from 1 h to 3 h. The surface wettability of the untreated/HMDS treated silica films was observed by measuring the WCA of the films. The variation of WCA with HMDS concentration and silylating period is shown in Fig. 1a–g. It is seen that silylation in 2.5–15 wt% for 1–3 h treatment time changed the surface characteristics of the unmodified silica films from hydrophilic (66 ± 2°) to hydrophobic (95 ± 3°–125 ± 4°). It was observed that even for 1 h treatment with 2.5 wt% HMDS, the surface became hydrophobic (~95 ± 3°) and for 3 h treatment the increase was more dramatic (from 66 ± 2° to 109 ± 4°) as shown in Fig. 2. As the HMDS concentration increased, there was a rapid enhancement in contact angle values even after 1 h treatment. Mostly all the WCA values raised with increase in HMDS concentrations as well as treatment time. The reason for increase in WCA is due to silylation taking place on the surface, where the –Si–OH groups get replaced by –Si–$(CH_3)_3$ groups as shown in reaction mechanism 4. There are reports in literature where FTIR studies have been carried out on silica surfaces modified by different silylating agents like trimethylchlorosilane [6], HMDS and hexamethyldisiloxane (HMDSO) [9]. The unmodified silica surfaces showed absorption peaks at 3400 cm^{-1} and 1050 cm^{-1}, characteristic of Si–OH groups and due to asymmetric stretching and vibration of Si–O–Si bonds respectively. The HMDS/HMDSO modified surfaces showed absorption bands around 2950 and 1400 cm^{-1} due to stretching and bending of C–H bonds along with peaks around 847 cm^{-1} due to the Si–C bonds. Except for slight increase in WCA with increase in treatment time and HMDS concentration, beyond 10 wt% HMDS treatment, almost saturation in WCA angles ~120–130° was observed. This is an indication that all the active sites (–Si–OH) on the surface have been replaced with –Si–$(CH_3)_3$ groups. A further increase in treatment concentration could lead to the reverse of reaction mechanism 4 taking place, which is evidenced by a slight decrease in the average WCA. The driving force for the reverse reaction to take place could be the steric hindrance caused due to the large number of –CH_3 groups on the surface.

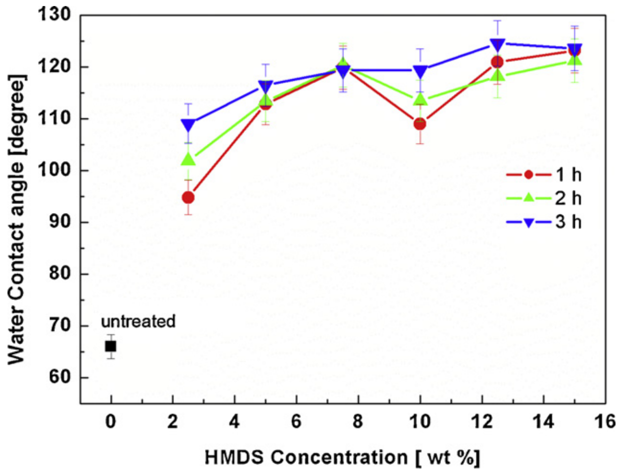


Fig. 2. Effect of concentration of HMDS and varying treatment times on water contact angle.

When the HMDS treated surfaces were heated to 150 °C for 1 h and WCA measured, they were found to be the same as obtained after room temperature drying of treated surfaces. This indicates that such hydrophobic coatings were possible to be generated even at room temperature. The images of water drops on surface of coatings derived from HMDS + silica sol after spray and dip coating are shown in Fig. 1h and i respectively. It was seen that after spray coating, the surface had become superhydrophobic and water droplets were found to roll from the surface when dispensed. The dip coated surface also exhibited hydrophobicity. The reason for difference in hydrophobicity when silica films are treated with HMDS and films formed from direct addition of HMDS to the silica sol is explained based on difference in surface morphology, as discussed in the following section.

3.3. Surface morphology

The surface morphology study for coatings generated from HMDS + sol, untreated silica coated SLG and HMDS treated silica coated SLG was carried out using the SEM analysis. The SEM images of untreated and HMDS treated silica films on SLG as shown in Fig. 3a and b did not show much difference when observed over the magnification range from 0.5k× to 60k×. Since the silica films were only chemically modified by HMDS on the surface by introduction of methyl groups, there was no distinct microstructural difference on untreated and HMDS treated surface. The HMDS treated surfaces exhibited a maximum WCA of ~130°. This observation is a proof of fact that chemically modified surfaces reach a saturation level of hydrophobicity.

As for the HMDS + silica sol, the SEM images depicted Fig. 3c and d show a porous surface morphology with many silica particles. These particles tend to trap the air in the pores of the films contributing to the higher water contact angle, which causes easy rolling of water drop on the surface and gives the water contact angle of 166 ± 4° and 145 ± 2° for spray and dip coated films respectively. Conventionally, superhydrophobic surfaces are produced mainly by two methods: one is to create a rough structure on a hydrophobic surface and another is to modify a rough surface with low surface free-energy materials. In the case of direct addition of HMDS to the silica sol, the situation is similar to modifying a rough surface formed by silica particles with silylating agent that produces low surface free energy. Such surfaces can be represented according to the Cassie–Baxter model [17] where air trapped within the microscale particles reduces contact area between water drop

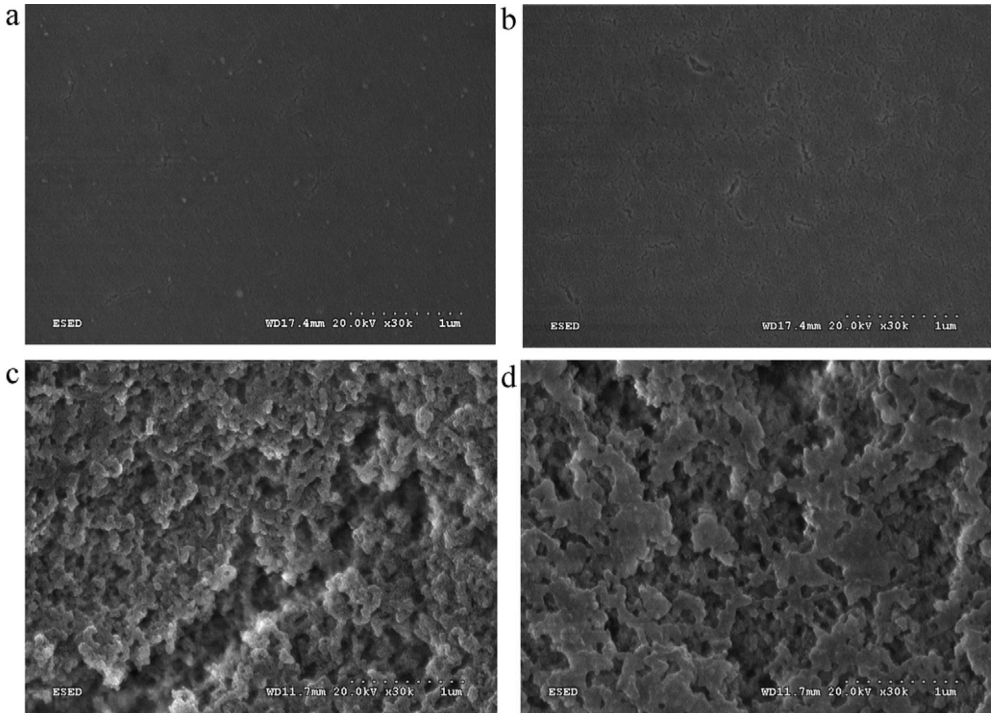


Fig. 3. Surface morphology of (a) untreated silica film; (b) 7.5 wt% HMDS treated silica film – 3 h and HMDS + silica sol: (c) spray and (d) dip coated.

and the surface, according to the equation:

$$\cos\theta^* = -1 + \Phi_s(\cos\theta + 1) \qquad (7)$$

where θ^* and θ are the contact angles with and without (i.e. on a flat surface) considering air trapping and Φ_s is the area of the liquid–solid interface over the area of the whole nominal interface. The Cassie–Baxter model assumes that a droplet is suspended on the rough structures and allows air trapping between the rough structures on a surface underneath the droplet.

3.4. Optical properties

Optical transmission of the bare, untreated silica coating, HMDS treated silica coating and spray coated HMDS + silica sol on SLG substrates were measured and are depicted in Fig. 4.

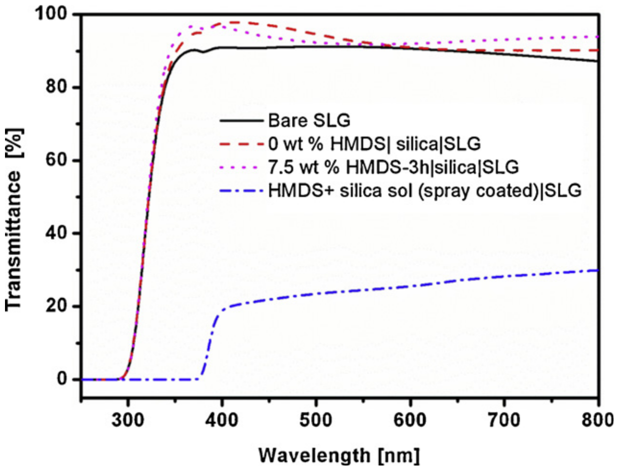


Fig. 4. UV–visible spectra for bare and various coated substrates.

The average transmission over 400–800 nm for the bare SLG, untreated silica coating, 7.5 wt% HMDS treated silica coating for 3 h and spray coated HMDS + silica sol coating were 90, 92 and 93 and 26% respectively. The HMDS surface modified silica coating showed slightly higher transmittance than an unmodified coating. The reason for the slight enhancement in transmission could be due to slight increase in porosity of the HMDS modified silica coating, since there is no cross-linking on the surfaces because of the presence of several non-hydrolyzable methyl groups. This small increase in porosity could lead to lowering of refractive index of the coating, which could increase the average transmission over the visible wavelength range. The transmittance spectra for the untreated and HMDS modified coatings show the presence of maxima between 350 and 550 nm. Typically for single layered coatings, a sinusoidal shape with a single maximum at a wavelength corresponding to the quarter-wave thickness occurs over the wavelength range of 400–800 nm could be expected. Since in the present investigation, the thicknesses of untreated and HMDS treated silica films were of the order of 0.3–0.4 μm, this is the reason for the occurrence of the maxima between 350 and 550 nm in the transmittance spectra.

Coatings derived from spray coated HMDS + silica sol however show very low transmission, though the magnitude of hydrophobicity was substantially higher than the HMDS treated silica coatings. The spray coating was carried out in such a way that the whole SLG surface was completely wetted with a continuous film. In this case, since silica particles formed are surface modified by HMDS, these surface modified particles form the coating, which induces some roughness to the coatings. The silica particles induces scattering of light and thereby decreases the intensity of transmitted light.

The pencil scratch hardness for untreated and silica films treated with HMDS were determined to be 5H, ''B or 2B'' respectively according to the concentration of the silylating agent used. The unmodified silica coatings were more scratch resistant due to the pure inorganic nature of the coating. In case of HMDS treated silica coatings, as the hydrophobicity was enhanced due to increase in HMDS concentration or treatment time, the pencil hardness decreased due to the hybrid nature of the coating arising due to presence of several low molecular weight methyl groups on the surface, which makes the films softer. In case of spray coated HMDS + silica sol, the pencil hardness reduced further to 7B due to poor adhesion of the films formed due to the HMDS modified silica nanoparticles on the surface.

The hydrophobicity (which is a function of surface roughness), transparency and scratch hardness of coatings are all competitive properties and mostly, one property is enhanced at the cost of another.

4. Conclusion

Surface modification of silica coatings derived from TEOS has been studied using two methods. One was by treating the silica surface with a silylating agent HMDS. The other was by adding silylating agent to silica sol, where superhydrophobicity was also obtained. In the first case, the static contact angles increased from $66 \pm 2^\circ$ for an untreated silica surface to $125 \pm 4^\circ$ after the treatment with HMDS. The HMDS treated films were transparent, adherent and thermally stable at least up to 150 °C. In case where coatings were generated using sols obtained by direct addition of HMDS to the silica sol, WCA varied from $145 \pm 2^\circ$ to $166 \pm 4^\circ$ for dip and spray coated surfaces respectively. The experimental results showed that a simple method of sol–gel process resulted in hydrophobic silica films without using fluoroalkyl compounds. The formation of non-fluorinated hydrophobic surface at low temperature is important for the fabrication of enviromental friendly coating for practical applications. The present investigation also indicates promise of generating stable hydrophobic surfaces using HMDS treated silica films from TEOS as precursor.

Acknowledgement

The authors gratefully acknowledge Dr. G. Sundararajan, Dr. G. Padmanabham, for providing constant support throughout the course of the investigation. The authors also thank L. Venkatesh for SEM analysis and to A. Ramesh for technical support.

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