Preparation of Water Repellent Layer on Glass Using Hydrophobic Compound Modified Rice Hull Ash Silica

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ABSTRACT

In this study water repellent layered glass has been prepared by coating silica (SiO_2) combined with a hydrophobic silane compound. SiO_2 was extracted from rice hull ash and two silane compounds, namely hexadecyltrimethoxysilane (HDTMS) and trimethylchlorosilane (TMCS) were used. Coating was performed through two deposition techniques, i.e. one step (mono-layer) and layer by layer (LBL, multi-layer). The effect of silane to SiO_2 mole ratio, silane type and layer number on the glass characters was evaluated. Characterization included hydrophobicity, transparency, surface roughness and stability of coating. Results showed that increasing the mole ratio of silane to SiO_2 and the layer number increased the hydrophobicity of the glass surface. The optimum mole ratio was 5:1 and the significant increase of contact angle occurred at lower mole ratio, but the stability tends to be increased at higher mole ratio. For HDTMS-SiO_2 layer, the technique of LBL technique produced a coating with higher hydrophobicity and transparency than single-stage one. The LBL technique produced the highest water contact angle of 103.7° with transmittance of 96%, while for TMCS-SiO_2 layer the one stage technique produced hydrophobic layer with higher water contact angle of 108.0° and transparency about 94.52%. The prepared hydrophobic glasses were relatively stable in polar and non-polar solvents, but unstable to ambient conditions.

Keywords: *rice hull; transparent; silica; water repellent; self-cleaning*

ABSTRAK

Pada penelitian ini telah dihasilkan kaca anti-air yang diperoleh melalui pelapisan silika (SiO_2) dan senyawa hidrofobik pada permukaan kaca. Prekursor yang digunakan adalah SiO_2 dari abu sekam padi dan dua jenis senyawa hidrofobik, yaitu heksadesiltrimetoksisilan (HDTMS) dan trimetilklorosilan (TMCS). Deposisi dilakukan dengan dua teknik yaitu teknik satu tahap (mono-lapis) dan layer by layer (multi-lapis). Teknik deposisi yang menghasilkan lapisan dengan hidrofobisitas dan transparansi tertinggi digunakan untuk mengkaji pengaruh rasio mol silan: SiO_2, jenis silan dan pengaruh jumlah lapisan. Karakterisasi kaca meliputi hidrofobisitas, transparansi, kekasaran permukaan dan kestabilan lapisan. Hasil menunjukkan bahwa peningkatan rasio mol silan: SiO_2 meningkatkan hidrofobisitas permukaan kaca dan mencapai titik optimal pada rasio mol silan: SiO_2 5:1. Peningkatan sudut kontak secara signifikan terjadi pada rasio mol silan: SiO_2 rendah, dan cenderung stabil pada rasio mol yang lebih tinggi. Pada HDTMS-SiO_2 teknik deposisi lapis celup layer by layer menghasilkan lapisan dengan hidrofobisitas dan transparansi lebih tinggi dibanding teknik satu tahap. Teknik deposisi layer by layer menghasilkan sudut kontak air tertinggi sebesar 103,7° dengan transmitansi sebesar 96%. Pada TMCS-SiO_2, teknik deposisi lapis celup satu tahap menghasilkan film hidrofobik yang lebih tinggi dengan sudut kontak air 108,05° dan transparansi sebesar 94,52%. Lapisan silan-SiO_2 relatif stabil pada pelarut polar maupun non polar, namun tidak stabil terhadap kondisi lingkungan ambien.

Kata Kunci: *sekam padi; transparan; silika; anti-air; self-cleaning*

INTRODUCTION

Self-cleaning glasses have attracted great interest because the glass is able to keep the surface free from dirt. Many companies have commercialized those products of technology to be used for daily life. Basically, self-cleaning can occur in hydrophilic and hydrophobic surface of glasses. Both may clean the

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surface by different behavior toward water [1]. The mechanism of hydrophilic self-cleaning is based on the photocatalytic effects, in which photocatalyst chemically breaks down the dirt under sunlight exposure. Hydrophobic self-cleaning, however, creates the spherical water droplets thereby they are easy to roll over the surfaces and carry the dirt away. In fact, hydrophobic surface shows more advantageous than hydrophilic surface because the cleaning performance of hydrophilic surface depends on sunlight exposure, while the hydrophobic surface is independent of sunlight exposure, so it can clean anytime.

Many articles reporting preparation of hydrophobic glass have been published [1-3]. Polymer, surfactant, long chain organic and silane compounds are commonly used to produce hydrophobic surfaces. Among various materials, silane compounds have been widely applied to coat glass surfaces because of its coupling agent properties. The compounds react with -OH groups on the silica surfaces. The type of silanes and the effect of hydrolyzed group amount on hydrophobicity have been studied [4-6]. Many authors reported that coating glass surface using hexadecyltrimethoxysilane (HDTMS) and trimethylchlorosilane (TMCS) increase the hydrophobicity [6-9].

The mechanical durability of the coating is also an important criterion for many applications. The coating prepared from SiO_2 demonstrates higher scratch resistance than bare substrate. Latthe and co-workers [10] stated that even rubbed with fingers, the coated material is not easily removed. However, the mechanical durability decreased with the higher concentration of SiO_2 due to the increase of layer thickness. Yan et al. [11] also used a layer of SiO_2 as pre-coating on the surface. When silane was coated onto the glass surface directly, the layer of silane would be removed from the surface easily. The possible reason is that there is no enough of Si-OH bonds on the glass surface. Addition of tetraethyl-ortho-silicate (TEOS) may enhance the number of Si-OH bonds. With TEOS, dense membranes are formed and more Si-OH bonds are created. In this condition, the silanes are strongly bonded to Si-OH on the glass surface. Hwang and Ahn [12] dispersed the powder of SiO_2 nanoparticles and coated in first layer of glass surface. This technique enhances the surface roughness and therefore the water contact angle of the surface increases. However, it does not increase the mechanical durability because the SiO_2 powder is difficult to attach strongly on the surface. Therefore, to achieve high mechanical durability, SiO_2 is coated via sol process.

Beside commercial precursors, silica may be extracted from rice husk ash, fly and bottom ash, bagasse ash, among others. Rice husk ash contains silica for about 87–97%, and can be used as a precursor to produce silica gel, sodium silicate, and amorphous silica [13]. Many authors have reported the use of rice husk ash in many applications [14-16]. In the present research, we prepared two types of silane compounds modified silica, SiO_2-HDTMS and SiO_2-TMCS, coated on glass surfaces. In this work, HDTMS and TMCS were evaluated to study the influence of long chain silane. Some of researches stated that the longer chain silane increase the hydrophobicity [6]. However, another study stated that short chain silane demonstrated higher water contact angle than longer one. It is probably due to the type of polymerization of short chain silane that was intermolecular silane coupling [17]. The characteristics of SiO_2 from rice husk ash, the influence of mole ratio of SiO_2 to silanes, the type of deposition and the number of layers coated were investigated and evaluated as well. Additionally, the characteristics of hydrophobic glasses were investigated through water contact angle, transparency, and their stability toward ethanol and hexane.

EXPERIMENTAL SECTION

Materials

The rice husk sample was collected from Bantul-Yogyakarta. NaOH, HCl, and ethanol were purchased from Merck. TMCS and HDTMS were purchased from Sigma Aldrich. The glasses used were commercial microscope slides with the size of 25 × 12.5 × 1 mm.

Instrumentation

X-ray diffraction (Shimadzu XRD 6000) was employed to detect the structure of rice husk ash. The functional groups were recorded with infrared spectrophotometer (Shimadzu Prestige 21). The optical transmittance of glass was carried out with UV-Vis spectrophotometer (Shimadzu UV-2401 (PC). The roughness of coated glass surface was determined by atomic force microscope (Bruker N8 NEOS). The wettability of coatings was evaluated by measuring of contact angle using ImageJ software.

Procedure

Preparation of sodium silicate from rice husk ash

The preparation procedure of sodium silicate was adopted from previously reported work [13]. Rice husk was heated at 700 °C for 4 h and the rice husk ash obtained was washed with 4 M HCl solution. The residue was neutralized, filtered, washed with distilled water and then dried at 100 °C for 2 h. The dried sample was sieved 200 mesh in size and characterized with XRD and infrared spectrophotometer. Ten grams of rice husk sample was added into 158 mL of 4 M NaOH solution under stirring for 4 h. The product obtained was specified as sodium silicate solution.

Coating of hydrophobic glass with HDTMS modified SiO_2 and TMCS modified SiO_2

Before coating, the glass slides were ultra-sonicated subsequently with distilled water, 5 M HCl solution, and ethanol for 10 min. The surface was then dried in the vertical position. In this work, the mole ratio of silane to SiO_2 was varied (0:1), (1:1), (3:1), (5:1), and (7:1) for two types of silane compounds. Two deposition techniques were also studied using one layer (OL) and layer by layer (LBL). LBL coating was held using two pots of solution (sol of SiO_2 and silane). Sol of SiO_2 was prepared by a mixing a 10 mL of sodium silicate solution and 200 mL of distilled water. Hydrophobic silane sol was prepared through dilution of silane compound in ethanol and stirring it for 2 h. For LBL technique, the cleaned glass was immersed in SiO_2 sol for 1 h, withdrawn with a speed of 3 cm/min and dried at 120 °C for 2 h. After that, similar work was conducted by dipping the SiO_2 coated glass into silane sol. Meanwhile, for OL technique the cleaned glass was dipped once in mixture of SiO_2 and silane sol.

RESULT AND DISCUSSION

Characteristics of SiO_2 from Rice Husk Ash

The hydrophobic glass was produced by two steps, i.e. preparation of sodium silicate from rice husk ash and coating of SiO_2-silane sol on the glass surface. In the first step, the characterization of SiO_2 from rice husk ash was introduced with FTIR spectrophotometry and XRD. The characteristic peaks are obtained at wavenumbers of 802, 1095, and 3418 cm^{-1}. An absorption peak at 802 cm^{-1} is assigned to the Si-O-Si bending vibration from SiO_2. Peak at 1096 cm^{-1} is related to the stretching vibration of tetrahedral Si-O. The absorption band at 3418 cm^{-1} is attributed asymmetric vibration of –OH from Si-OH. The x-ray diffraction pattern of rice husk ash. It shows a hump peak in 2θ = 20–22° indicating the amorphous structure of silica. The characters found are similar to results reported by Kalapathy et al. [18].

Water Contact Angle and Transparency of Silane-SiO_2 Coated Glass

The surface of glass becomes hydrophobic and the water molecules are repelled when the surface

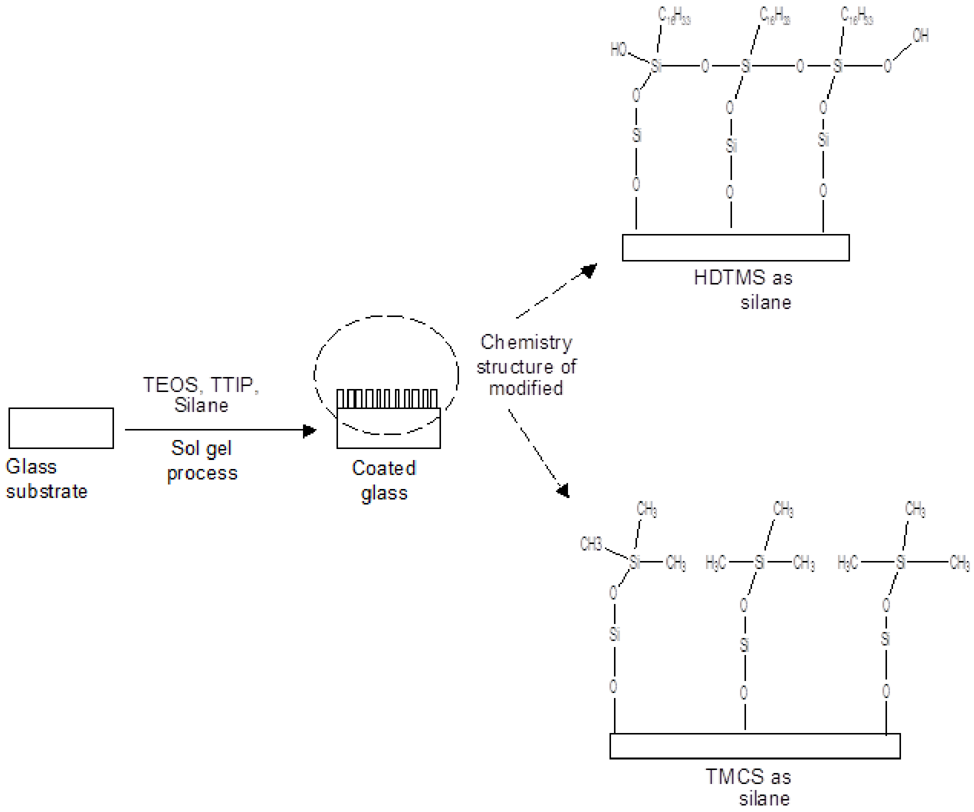

Fig 1. Scheme of chemical structure of prepared hydrophobic glass surface

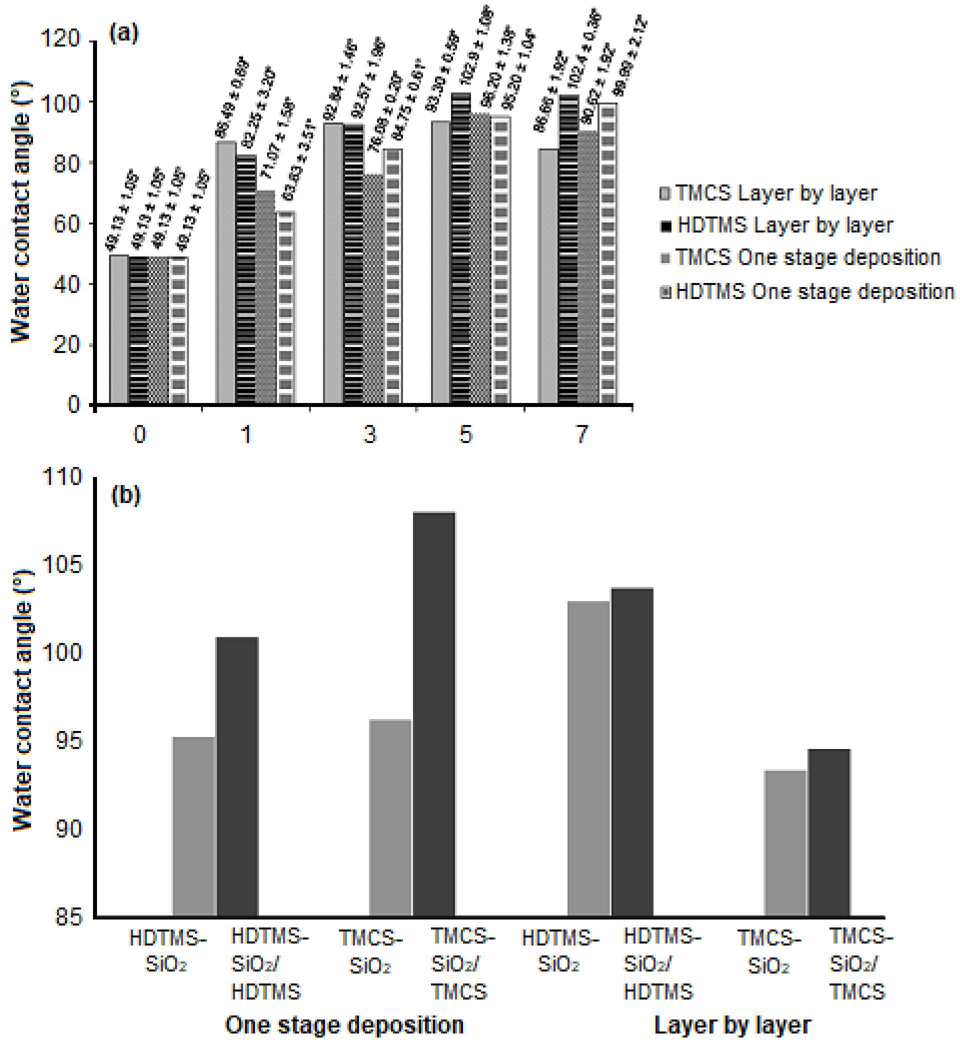

Fig 2. The influence of (a) silane concentration in mole (SiO_2 1 mole), and (b) type of coating towards water contact angle at the molar ratio of silane to SiO_2 5:1

chemical modification is made. It can be achieved by the addition of alkysilanes or alkylchlorosilanes in the glass surface since they have at least at one hydrolysable group along with one or more non-hydrolysable groups [6]. In this research, silane compounds of HDTMS and TMCS were used as the hydrophobic sources. Since the Si–OCH_3 groups of HDTMS and Si-Cl of TMCS are hydrolysable, they react with the OH groups through the formation of -Si-O-Si-, releasing H_2O, and to form the hydrophobic surface. Fig. 1 displays the scheme of the hydrophobic glass preparation.

Fig. 2 shows the data of water droplet on the prepared hydrophobic glass with variation ratio silane to SiO_2 from 1:1 to 7:1. Glass was immersed in the hydrophobic solution using OL deposition. Both of HDTMS-SiO_2 and TMCS-SiO_2 demonstrate that the hydrophobicity is enhanced proportionally to the molar ratio of silane to SiO_2 from 1:1 to 5:1. At the ratio of silane to SiO_2 of 5:1, the water contact angle of HDTMS-SiO_2 is 95.2°. At the same ratio, TMCS-SiO_2 generates water contact angle of 96.2°. The increase of contact angle might be due to the substitution of the polar –OH groups in the surface by the non-polar –CH_3 groups of HDTMS and TMCS, respectively. However, the water contact angle decreased at the silane to SiO_2 ratio greater than 5:1. It is probable that not all of silanes interact with SiO_2. Addition of silane layer as the second layer in the coated glass is able to enhance the hydrophobicity. Due to the second deposition of silane, the water contact angle HDTMS-SiO_2 and TMCS-SiO_2 increased to become 100.9° and 108.05°, respectively. This increase of water contact angle is attributed to the rough surface because of the increasing number of hydrophobic layer [19].

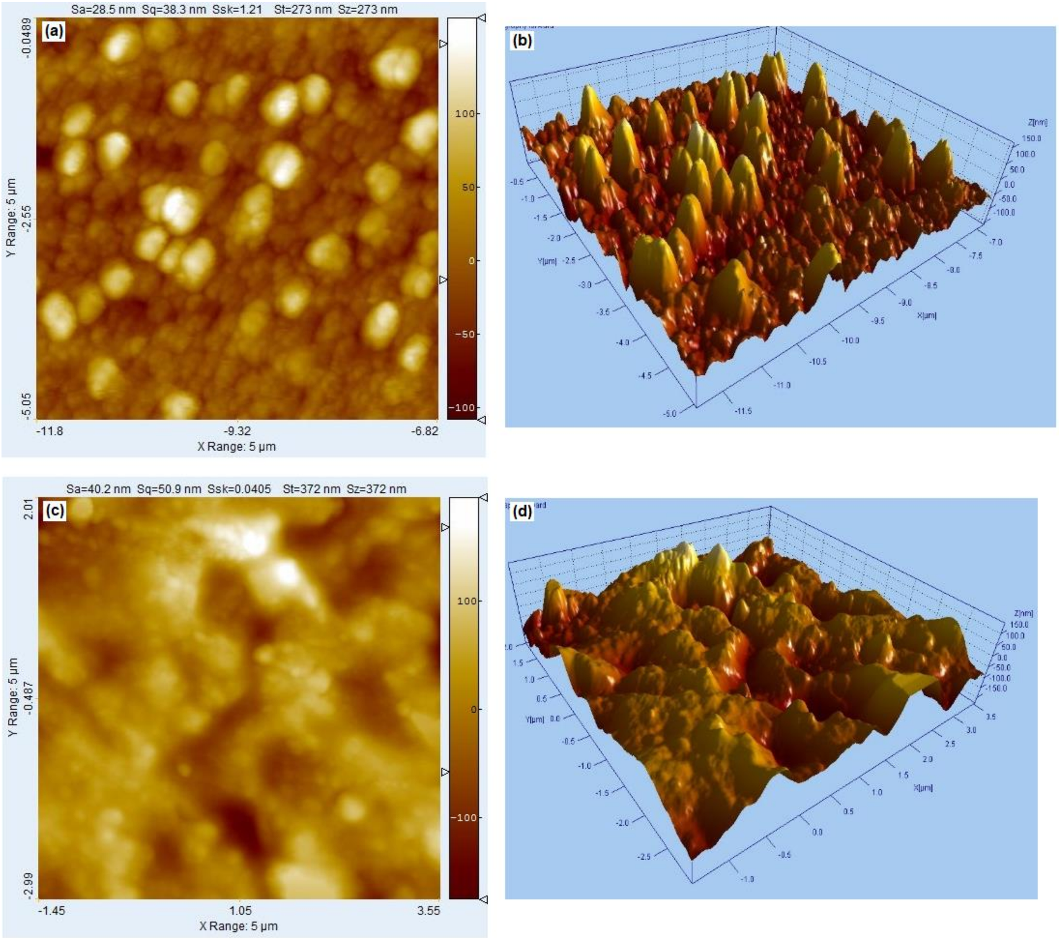

Fig 3. AFM analysis of HDTMS-SiO_2 coated glass with coating technique: (a-b) one stage deposition, (c-d) layer by layer

As a comparison, the influence of coating type was evaluated. The prepared glass was immersed with two coating type, OL and LbL. OL coating was prepared through deposition of coating solution in one pot (one stage deposition) while LbL coating was prepared by two pots of sol, i.e. SiO_2 and silane. The water contact angle of HDTMS-SiO_2 coated glass using OL was only 95.2 ± 1.4°, and that using LbL was 102.9 ± 1.1°. The type of coating was predicted to influence the surface roughness. To confirm this hypothesis, we analyzed the surface topography using AFM. The AFM measurement of coated glass is shown in Fig. 3. The root mean square (RMS) and average roughness (Sa) value of HDTMS-SiO_2 coated glass were 38.3 and 28.5 nm for OL and 50.9 and 40.2 nm for LbL, respectively. Similar observation was also obtained by Rios et al. [20]. Mohamed et al. [2] stated that LbL deposition offers a high degree molecular control on the surface. It should be concluded that HDTMS as outer layer in LbL presents higher hydrophobicity than OL deposition technique.

The transparency is one of the important properties in the glass coating. It is known that the deposition technique influences the optical properties of glass. Glass was coated using TMCS-SiO_2 through OL deposition, resulted the transmittance of 65.13%. While, LbL deposition technique exhibited the transmittance about 94.81%. The low transmittance of SiO_2-TMCS through one layer deposition is due to the formation of white suspension when TMCS and SiO_2 was mixed. The increase of film thickness also caused the decrease of the transmittance [21].

The Stability of Hydrophobic Coating on the Glass Surface

Many researchers have studied the stability of hydrophobic coatings on many substrates in various organic solvents [2]. The stability of hydrophobic surfaces in ambient temperature is also an important factor. In this work, the stability of coated glass was conducted by measuring the change of water contact angle toward ethanol and hexane as the solvents at ambient temperature. The contact angle of HDTMS-SiO_2 and TMCS-SiO_2 were decreased insignificantly for 120 min of immersion time under ethanol and hexane. It could be concluded that both of them demonstrate high stability toward the solvents. However, both of them are unstable at ambient temperature. The outdoor exposure for 10 days decreased their water contact angle. The water repellent capability of hydrophobic coatings gradually degrades during long-term outdoor exposure and contaminant accumulation. This might be due to the presence of a moisture adsorption from the atmosphere by the polar –OH bonds in silica coating [22]. It is supported by the previous research stating that constructing hydrophobic glass using sol-gel technique has poor moisture resistance due to the existence of hydroxyl group [23].

We propose that HDTMS and TMCS have similar stability because of their similar surface interaction. Monofunctional organosilanes such as TMCS have one possibility of surface attachment, namely covalent interaction. Trifunctional organosilanes contribute three possible interactions, namely self-assembly (horizontal polymerization), covalent attachment, and vertical polymerization. However, long alkyl chain length creates covalently attached monolayers because the bulky molecule hinders it to arrange the horizontal and vertical polymerization. The covalent attachment produces smooth surfaces [24]. Therefore, we conclude that the difference of chain length ($C_{16}H_{33}$ of HDTMS and $(CH_3)_3$ of TMCS) and amount of functional group (tri-hydrolysable group of HDTMS and mono-hydrolysable group of MTMS) do not influence the hydrophobicity and stability of coated glass.

Comparing to the type of deposition, the surface produced with OL technique showed higher stability than that with LbL. The optimum concentration ratio of HDTMS/SiO_2 and TMCS/SiO_2 was about 5:1. In other words, there is no enough Si-OH group from SiO_2 to bond silane and the glass surface. In the LbL deposition, the amount of silane attached on the surface directly was higher than that attached on the Si-OH bonds of SiO_2. It causes the silane to be removed from surface easily. In case of OL deposition, the self-assembly of molecules is likely to occur. The molecular arrangements are held by themselves. Hence, they produce the stable system and minimize the steric effect. It is confirmed by the higher stability of OL than LbL deposition.

CONCLUSION

Water repellent glasses have been synthesized using SiO_2 from rice husk ash and silanes of TMCS and HDTMS. The hydrophobic glass with molar ratio of HDTMS to SiO_2 and TMCS to SiO_2 of 5:1 giving water contact angle of 95.2 and 96.2°, respectively. The addition of silane as the second layer improved the hydrophobicity of HDTMS-SiO_2 and TMCS-SiO_2 to 103.07° and 108.05°, respectively. High optical transmittance was found using layer-by-layer technique. Both of HDTMS-SiO_2 and TMCS-SiO_2 exposed high durability toward ethanol and hexane, but unstable at ambient temperature.

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