Organic plasma-polymer thin film coatings on Super-hydrophilic coated surface for increasing the surface durability against scratch without changing of surface wettability

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Abstract. In this study, the SiO polymer coating film was prepared containing tetraethyl orthosilane (TEOS) solution by the sol-gel method on soda lime glass. After then, the plasma polymer coating was deposited on SiO polymer coated glass by plasma enhanced chemical vapor deposition (PECVD) method at room temperature during 15 seconds. The thiophene monomer was used as organic precursor. It was heat up to 60 °C and bubbled with hydrogen gas which flow rate was 50 sccm. Plasma was ignited by radio frequency (RF, 13.56 MHz) and its power was 10 W.

SiO polymer and plasma polymer coated SiO polymer films were investigated by Fourier Transform Infrared (FT-IR), scanning electron microscopy (SEM), ultraviolet-visible (UV-Vis.), water contact angle, the adhesion test, and the pencil hardness test. The IR spectra shows evidence of very thin organic plasma polymer, which could not be measured by SEM cross image. The SEM images show that the morphology of each film was not changed by plasma polymer coating. Low water contact angles showed with both coating. Moreover surface hardness was increased by plasma polymer coating.

Introduction

Glass is a material which plays an important role in architecture and in the automotive and display industries. The unique basic property for this application is its transparency combined with its complete impermeability to gases or liquids. In addition to this, a high stiffness is required for a variety of applications. However, for an increasing number of applications, additional properties are required which, for example, are focussed on the control of light transmission in a passive or even active way or to control surface chemistry in connection with impacts from environment (moisture, dust). For these reasons, coatings have to be developed to adapt or to vary glass properties for the desired purposes. The super-hydrophilicity of solid surfaces is an attractive topic in anti-fogging [1]. Nanostructured semiconductor materials have been the prime focus of scientific research [2] and [3] due to their unusual optical [4], chemical [5], photovoltaic [6] and electronic properties [7]. The wettability of surface is controlled by the surface energy and surface roughness. Increase of surface roughness would largely amplify both hydrophobicity and hydrophilicity [8]. Transparent super-hydrophilic self-cleaning TiO₂ coating films on glass substrates have high potentiality for practical applications such as mirrors, window glasses, windshields of automobiles, etc. The super-hydrophilic property of the surface allows water to spread completely across the surface rather than remain as droplets, thus making the surface anti-fogging and easy to wash. Recently, there have been some research papers about the super-hydrophilic property of TiO₂ coating films [9]. The degradation mechanism of the hydrophilicity of TiO₂ surface in the dark is still open to discussion. However, this phenomenon in the dark must be a problem to be overcome for a practical use. In order to keep the hydrophilicity effective even in the dark, therefore, SiO₂ has often been used as a hydrophilic material [10].
In this research, hydrophilic SiO polymer coated with CHxS topmost coating was mainly investigated without property changes for anti-fogging application with high surface hardness.

Experimental

This experiment is made up SiO polymer dip coating step and CHxS plasma polymer deposition step. Firstly, SiO polymer colloidal solution was prepared within TEOS by sol-gel method. And then SiO polymer was coated on soda lime glass by dip coating method. Dipping speed was 2 mm/sec. SiO polymer coating was dried in the air after the dip coating process. The CHxS plasma polymer thin films were deposited by PECVD method during 15 sec. Thiophene was utilized as organic precursor and preheated to 60 °C, and bubbled up by 50 sccm of hydrogen. The plasma polymer film thickness was approximately 5 nm. The deposition pressure and RF plasma power were $4.0 \times 10^{-1}$ Torr and 10 W.

The chemical bonding types of each sample were investigated by FT-IR (Bruker Optik, Vertex 70). Attenuated total reflectance (ATR) FT-IR was used to investigate the surface change in chemical bonding group. The surface morphology and cross sectional images were investigated by field emission (FE) SEM (JEOL, JSM6700F). Transmittance of each coating was measured by UV-visible spectrometer (Varian, CAry 5000). Wettability was measured by water contact angle measurement system (KSV instrument, attention). Also, the adhesion test and the hardness test were carried out by cross cut test and ASTM D3363 [11].

Results and discussion

Characteristics of each sample looks like the same by eyesight. Pencil hardness was 6H. Adhesion of each sample was also good (Table 1). Thus, following tests make sure the properties of each sample.

<table>
<thead>
<tr>
<th>Property</th>
<th>SiO polymer coated glass</th>
<th>CHxS plasma polymer on SiO polymer coated glass</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparency</td>
<td>Clearness</td>
<td>Clearness</td>
<td>Eyesight</td>
</tr>
<tr>
<td>Pencil hardness</td>
<td>5H–6H</td>
<td>&gt;6H</td>
<td>ASTM D3363</td>
</tr>
<tr>
<td>Adhesion</td>
<td>100/100</td>
<td>100/100</td>
<td>Cross cut test</td>
</tr>
</tbody>
</table>

Figure 1 shows the SEM images of SiO polymer coating and CHxS deposited on SiO polymer coating. Figure 1(a) is SiO polymer coated surface and fig. 1(c) is CHxS deposited on SiO polymer surface. Figure 1 (a), (c) shows the almost same morphology. It means that the ultra thin CHxS plasma polymer deposition did not affect the surface morphology. Also, figure 1 (b), (d) shows the almost same thickness. However, surface in figure 1(d) shows brighter than figure 1(b) because of electron charging effect. CHxS plasma polymer shows the characteristic of insulator [12] thus, thus electron charging effect occurred with CHxS deposition.

Figure 2 shows the FT-IR spectra of each sample. The chemical bonding of plasma polymerized thin films was analyzed using FT-IR absorption over a range of 4000–1000 cm$^{-1}$. The IR spectra exhibited an absorption band at 1050 and 1240 cm$^{-1}$, corresponding to a Si–O stretching vibration band. Moreover, absorption bands at 1380–1457, 1640, 1715, 2870–2960, and 3260–3660 cm$^{-1}$ corresponded to Si–CH3, C=–C, C=S, CHx (stretching vibration mode), and OH bands, respectively [13]. The CHx band (2870–2960 cm$^{-1}$) showed up with only CHxS plasma polymer deposition. From the IR result, CHxS plasma polymer layer was successfully deposited with 10 watt of RF power.

Figure 3 shows transmittance (%) of soda lime glass, SiO coated glass, and CHxS deposited on SiO coated glass. Transmittance of each sample was higher than soda lime glass. However, transmittance of UV and IR region was decreased by CHxS plasma polymer coating.
Figure 1. SEM images of (a), (b) before and (c), (d) after the CHxS deposition on SiO polymer coating.

Figure 2. FT-IR spectra before and after the CHxS deposition on SiO polymer coating.

Figure 3. UV-vis. spectra of each sample.

Figure 4 shows water contact angle images of (a) soda lime glass, (b) SiO polymer coated glass, and (c) CHxS plasma polymer deposited on SiO polymer coating. Wettability was increased by SiO polymer coating. Also, CHxS plasma polymer deposition help to increase water contact angle due to without surface roughness change.

Figure 4. Water contact angle images of (a) soda lime glass, (b) SiO polymer coated glass, and (c) CHxS plasma polymer deposited on SiO polymer coated glass.

Figure 5 shows the optical microscope images of (a) SiO polymer coated glass and (b) CHxS plasma polymer deposited on SiO polymer coated glass. Vague lines shows in center of Fig. 6(a), which was produced by pencil hardness test. It was pointed by arrow mark. However, no line was produced by pencil test with 6H, which was deposited with CHxS plasma polymer on SiO polymer coated glass as shown in Fig. 6(b).

Figure 5. Optical microscope images of (a) SiO polymer coated glass and (b) CHxS plasma polymer deposited on SiO polymer coated glass.
Summary
SiO polymer coating was carried out dip-coating method and CHxS plasma polymer coating was carried out plasma enhanced chemical vapor deposition within homemade stainless steel vacuum chamber. Each coating was successfully formed on glass or SiO polymer layer. Evidences of deposition were investigated by ATR FT-IR, SEM, and UV-visible experiments.

The hardness of SiO layer was reinforced in surface hardness by CHxS ultra thin layer without large change of optical property and wettability. Moreover, corrosion effect was expected within CHxS plasma polymer coated SiO polymer [14]. Thus, CHxS layer is applicable for the life protection of SiO polymer coating in general usage.

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References
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10.4028/www.scientific.net/AMR.415-417.1879