Effect of Methyl Triethoxysilane on Properties and Structure of Porous Silicate Antireflective Coatings

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Abstract: A porous silica anti-reflective (AR) coating was fabricated by a acid catalyzed sol-gel process with tetraethoxysilane (TEOS) as a precursor, methyl triethoxysilane (MTES) as an organic modifier and Triton®X-100 as a sacrificial template. The effect of MTES on the properties and structure of porous SiO\(_2\) antireflective coating was investigated. The results indicate that the hydrophobicity of the coating increases with the increase of MTES, and the contact angle of the coating increases from 11° to 94° when a mole ratio of MTES to TEOS changes from 0:1 to 2:1. The pore size in coating is between 20 to 30 nm at a small amount of MTES in the coating (i.e., a mole ratio of MTES to TEOS is 0:1). The proportion of the pores with the size of 20–30 nm increases and some pores with the size of 30–40 nm appear when a mole ratio of MTES to TEOS is 1:2. At a mole ratio of MTES to TEOS of 2:1, the proportion of pores with the size of 20–30 nm increases and the number of pores with the size of 30–40 nm decreases. The condensation resistance of coating firstly increases and then decreases slightly with increasing the MTES. The results indicate that the pore size in coating induced due to the addition of MTES has an effect on the coating performance like the condensation resistance rather than the hydrophobicity. At a mole ratio of MTES to TEOS of 1:2, the coating has the superior performance (i.e., the transmittance of coating is 5.58%, the abrasion resistance is 0.25%, and the condensation resistance is 0.12%).

Key words: tetraethoxysilane; methyl triethoxysilane; silicate; porous antireflective coatings; condensation resistance
1 Introduction

As solar photovoltaic technology becomes popular as a clean energy technology, the photovoltaic component is widely used. However, the lower conversion efficiency restricts the use of the existing photovoltaic component. Many efforts have been dedicated to improving the conversion efficiency, and the antireflective (AR) coating on solar cover glass is one of the most effective means.

Porous silica coating is usually chosen for the AR coating on solar glass of photovoltaic components due to its low refractive index and mechanical stability. [1-5] However, pure inorganic porous silica coating absorbs moisture in air at a high humidity due to the abundant hydroxyl group in the micro-pore structure of coating, leading to the decrease of the transmittance of the solar glass coated with the AR coating and the conversion efficiency. This is so-called condensation phenomenon. Some solutions to this problem were reported. [6-7]

Guillemot, et al. [6] investigated to enlarge the diameter of pore structure to reduce the condensation phenomenon on coating. They prepared the mesoporous AR coatings via the removal of large polymer nanoparticles during heat treatment, having that the coatings with the pores of > 30 nm exhibit the superior condensation resistance performance. Vicente, et al. [7] used hydrophobic compound hexamethyldisilazane (HMDS) to modify the coating surface, which has the contact angle (CA) in water of 100°.

In this paper, porous anti-reflective silica coatings were prepared with Triton®X-100 as a porogen and tetraethylorthosilicate (TEOS) and methyl triethoxysilane (MTES). The effect of MTES on the properties and structure of the AR coatings were investigated. The relationship between the structure of coating and its performance, especially condensation resistance, was discussed.

2 Experimental

2.1 Sample preparation

The sols were prepared by mixing MTES (purity is 99%, density is (885 ±5) mg/cm³, Hubei Liding Chemical Co., Ltd., China), TEOS (analytical reagent (A.R.), molecular is 208.33, Tianjin Guangfu Chemical Reagent Co., China), water and ethanol (A.R., Sinopharm Chemical Reagent Co., Ltd., China) at a mole ratio as x:1:3:48 (x equals 2.1, 1/2, 1/3, 1/4 and 0, respectively, for 6 solution samples). Hydrochloric acid (AR, Hangzhou Chemical Reagent Co., Ltd. China) was used as a catalyst. After stirring for 24 h, Triton®X-100 (the molecular mass is 636, Sigma-Aldrich) was added as a porogen at a concentration of 8% (mass fraction). The coatings were deposited on a float solar glass of 3 mm thickness (100 mm×50 mm, Xinyi Glass Group, China) by a dipping method. The withdrawal rate was adjusted to 20 cm/min to obtain the optimal thickness. Coating samples were immediately sintered in an oven at 500 °C for 15 min.

2.2 Characterization

The transmittance spectra of the samples were determined at room temperature by a model Perkin-Elmer DU800 ultraviolet-visible (UV-Vis) spectrophotometer. The thickness and refractive index were measured by a Ellip-A ellipsometer. The surface morphologies of the coatings were characterized by a multimode scanning probe microscope (SPM) in the mode of tapping. The static contact angle of the samples with water was measured by a KSV CAM 200 instrument. The pore structure of the dried coating solution powder was evaluated by a model ASAP2010 instrument (Micromeritics Co., USA) based on the principle of nitrogen gas adsorption-desorption.

The average transmittance of the samples is calculated, which is derived from solar direct transmittance (ISO 9050), by

$$\tau = \frac{\sum_{\lambda=380 \text{ nm}}^{\lambda=1100 \text{ nm}} \tau_{\Delta \lambda} s_{\lambda \Delta \lambda}}{\sum_{\lambda=380 \text{ nm}}^{\lambda=1100 \text{ nm}} s_{\lambda \Delta \lambda}}$$  (1)

where $\tau_{\lambda}$ is the wavelength-dependent transmittance of the coating and the factor $s_{\lambda \Delta \lambda}$ of different wavelengths can be listed in Table 2 (ISO 9845-1:1992).

The condensation resistance was characterized by the change of average transmittance of coating before and after being in an enclosed room with 90% RH for 48 h. The abrasion resistance was defined by the change of average transmittance of coating before and after being scratched by wool felt under 2.3 kPa according to the European standard EN 1096-2:2001.

3 Results and discussion

3.1 Properties of the AR coatings

Figure 1 shows the static contact angle of the coatings at different amounts of MTES. It is seen that the contact angle of AR coating decreases gradually from 93° to 11° with decreasing the amount of MTES. It indicates that the hydrophobicity of the coating increases with methyl group of MTES. Figure 2 shows the transmittance spectra of coatings at different amounts of MTES. The transmittance of coating is low in the absence of MTES (see bare glass in Fig. 2(f)). The transmittance of AR coating increases in the presence of MTES, and the maximum transmittance is 99.6% at 530 nm when the ratio of MTES to TEOS is 1:2.
coatings deteriorates, and average transmittance of coating increases, and condensation resistance of coating firstly increases and then decreases with increasing MTES. The optimum condensation resistance of coating is 0.12 at a mole ratio of MTES to TEOS of 1:2. It is also indicated that the optimum performance of the AR coating can be obtained at a mole ratio of MTES to TEOS of 1:2.

3.2 Microstructure of AR coatings with different amount of MTES

Figure 3 shows the SPM images of AR coatings surfaces at different amounts of MTES.

It is seen that the surface of coating becomes more rough when MTES increases.

Figure 4 shows the adsorption-desorption isotherms curves and their corresponding t-plot curves of different samples. It is indicated that the pore structure of the AR coatings belongs to the IUPAC type I, which corresponds to a micro-porous structure material. Some analogues of hysteresis loop that usually appear in mesoporous material are shown in Figs. 4(a) and 4(b). The t-plot diagram (see Figs. 4(d) and 4(e)) of the two samples shows that there are the massive mesopores with the diameter of 30–40 nm in the coating. However, a few mesopores appear in the sample without MTES. When a mole ratio of MTES to TEOS is 1:2, the proportion of the mesopores with the diameter of 30–40 nm in the coating is much more than that of other two samples. The results are exactly consistent with those from a previous work. The change of the refractive index is small. According to the Kelvin equation, the capillary condensation is related to the pore diameter. This can explain why the optimum condensation resistance of the coating appears when the ratio of MTES to TEOS is 1:2. The addition of MTES can result in the greater meso-pore structure to change the condensation resistance of the coating.

Table 1 Properties of coating samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>x</th>
<th>τ%</th>
<th>$R_{\text{AB}}$%</th>
<th>$R_{\text{CR}}$%</th>
<th>$\theta$(°)</th>
<th>H/nm</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2:1</td>
<td>5.25</td>
<td>0.52</td>
<td>0.34</td>
<td>93</td>
<td>103</td>
<td>1.25</td>
</tr>
<tr>
<td>B</td>
<td>1:1</td>
<td>5.64</td>
<td>0.31</td>
<td>0.22</td>
<td>78</td>
<td>113</td>
<td>1.28</td>
</tr>
<tr>
<td>C</td>
<td>1:2</td>
<td>5.58</td>
<td>0.25</td>
<td>0.12</td>
<td>65</td>
<td>111</td>
<td>1.34</td>
</tr>
<tr>
<td>D</td>
<td>1:3</td>
<td>5.12</td>
<td>0.19</td>
<td>0.39</td>
<td>37</td>
<td>107</td>
<td>1.37</td>
</tr>
<tr>
<td>E</td>
<td>1:4</td>
<td>4.46</td>
<td>0.16</td>
<td>0.49</td>
<td>26</td>
<td>110</td>
<td>1.36</td>
</tr>
<tr>
<td>F</td>
<td>0</td>
<td>4.13</td>
<td>0.10</td>
<td>2.10</td>
<td>11</td>
<td>105</td>
<td>1.39</td>
</tr>
</tbody>
</table>

x is mole ratio of MTES to TEOS; τ is average transmittance; $R_{\text{AB}}$ is abrasion resistance property; $R_{\text{CR}}$ is condensation resistance property; $\theta$ is contact angle; H is thickness; n is refractive index at 600 nm.
4 Conclusions

The AR coatings were prepared by a sol-gel method with TX-100 as a porogen and TEOS, MTES as precursors. The effect of the amount of MTES on the properties and structure of coating was investigated. The surface of AR coating became rougher and the more meso-pore structure with the pore diameter of 30 nm appeared in the coating when the amount of MTES increased. The decrease of the abrasion resistance of the coating led to the increase of the average transmittance. The optimum performance of AR coating could be obtained at the mole ratio of MTES to TEOS of 1:2.

Fig. 4 Nitrogen adsorption-desorption isotherms and t-plot diagram of the powders from AR coating solution with different with different mole ratios of MTES to TEOS

参考文献: