Preparation and Properties of TiNₓ-SiO₂ Antireflective Coatings with Print Process

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Abstract This paper describes the preparation and properties of TiNₓ-SiO₂ double-layered antireflective (AR) coatings that were applied with print process. The coating material was analyzed and TiNₓ was used instead of TiO₂ as high refractive material. The influence of solution concentration on AR property was studied. The testing result shows that the coatings using print process are featured with excellent mechanical property and the AR property is comparable to American Southwall AR product. It is expected that the study would promote the industrialization progress in AR coatings.

Key words TiNₓ, print process, AR coatings.

1 Introduction

TiNₓ coatings possess many good properties, such as high hardness, high melting point, abrasion resistant and erosion resistant[1,2]. It has been widely used as abrasion and erosion resistant layer in the fields of electronic engineering, machinery and so on. It is also used as adornment material due to its gold color. In the present paper, TiNₓ is analyzed as high index material in place of TiO₂ for the antireflective (AR) coatings.

For the sol-gel process, dip and spin process are often used to prepare coatings. In this paper, print process, traditionally used to print papers, plastics, etc., was applied to prepare coatings. With the advantage of the simple process and low cost, it is expected that the study would promote the industrialization of AR coatings via sol-gel technology and realize the scale production.

2 Experiment

Low index SiO₂-based solution was prepared in own lab, which comprised starting compound ethyl silicate (TEOS) (1 mol), alcohol (25 - 35 mol), de-ionized water (2 - 5 mol), KH550 (proper amount) and acid catalyst (0.05 - 0.1 mol). The regents above were C.P.

The process for preparing solution was simple. At room temperature TEOS was dropped uniformly into the alcohol solution and stirred for 30 minutes, then water was added and stirred for 30 minutes. Successively other reagents were added and stirred thoroughly for more than 60 minutes. Aging process was continued until the transparent SiO₂-based coating solution appeared.

In Fig. 1 the print process on the TiNₓ coated PET films was shown. The TiNₓ coated polyethylene terephthalate (PET) films were used as substrates, which were blue with grayish tint. They were cleaned by ultrasonic wave before the print process and dried to remove water. The films were fixed on the modified print machine, and the heating equipments were operated. At the rate of 15 cm/s, the SiO₂-based solution was coated on the films. The films were dried after printing immediately. To get good mechanical property, annealing process was operated after printing. During the print process, the printing/drying/annealing cycle was performed for one time and two-layered coating stacks were got. The optical and mechanical capacity tests were conducted on the AR coating stack and the corresponding properties were analyzed.

3 Results and Discussions

3.1 Properties of TiNₓ-SiO₂ coatings
Fig. 1 Flow diagram of print process

The detailed data for TiN\textsubscript{x}-SiO\textsubscript{2} AR coatings are shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
<th>Testing method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical reflect.</td>
<td>&lt; 1.0 %</td>
<td>Spectrophotometer</td>
</tr>
<tr>
<td>Transmittance\textsuperscript{1}</td>
<td>&gt; 67 %</td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>Purple</td>
<td></td>
</tr>
<tr>
<td>Tape adhesion</td>
<td>No peel off</td>
<td>Crosshatch tape test</td>
</tr>
<tr>
<td>Hardness</td>
<td>2H</td>
<td>Pencil scratch test</td>
</tr>
</tbody>
</table>

\textsuperscript{1} The air transmittance was assigned as 100% and the transmittance value in the table was obtained.

Among parameters, the hardness was measured by the pencil scratch test. It was performed according to the method B in GB/T6739-1996. In the study, the double-layered coating stack improved the hardness of substrate, and the hardness of blank PET film increased from HB to 2H. It attributed to the good physical property of coating material, especially to the TiN\textsubscript{x}’s excellent hardness. The adhesion property was analyzed by crosshatch tape test. It was proved that the adhesion of AR coating stack to PET substrate was excellent. It passed the crosshatch tape test and none was peeled off. It could be explained by the fact that in the TiN\textsubscript{x} and SiO\textsubscript{2} double-layered coating, there was a small quality of Si and Ti diffusing into each other’s side at their interface and Ti-O-Si (or Si-O-Ti) chemical bond formed in the layer’s interface region\textsuperscript{[3,4]}. The absolute reflection level of AR coatings was measured by UV/VIS/NIR spectrophotometer (Lambda 900), whose wavelength precision was less than 0.08 nm. The PET blank film was used as reference sample. Wavelength scan was performed at the range of 400 nm to 700 nm and the curve line is shown in Fig. 2. By comparison with that of the blank PET films, the reflection value of TiN\textsubscript{x}-SiO\textsubscript{2} coatings decreased sharply. At 540 nm the lowest reflection value was achieved and the average reflection value from 400 nm to 700 nm was below 1.0 %, about 2.0 % lower than that of the blank film. In the most of visible spectrum, from 420 nm to 660 nm, the reflection value was lower than 0.7 %, which was good for the optical material used in the visible spectrum.

The transmittance property was measured by VIS spectrophotometer (VIS7200), whose wavelength precision and luminosity precision were 1 nm and 0.8 % respectively. Wavelength scan was performed at the range of 400 nm to 700 nm and the results are shown in Fig. 3. By comparison with the TiN\textsubscript{x} coated films, TiN\textsubscript{x}-SiO\textsubscript{2} AR coatings had a good transmissivity. The average transmissivity from 400 nm to 700 nm was more than 67 %, which is about 7 % higher than that of TiN\textsubscript{x} coated film. It could be explained that the low index coating, SiO\textsubscript{2} coating, reduced the difference of the optical refractive index between air and the TiN\textsubscript{x} coated substrate. The reflection decreased and the transmittance of the film increased.

In the present study, the AR property of the prepared TiN\textsubscript{x}-SiO\textsubscript{2} coatings was compared with that of Southwall AR products. It was measured by single side reflection and the value was absolute. UV-1601 (model) UV spectrophotometer made by SHIMAZU was used. The result is shown in Fig. 4. It was clear that the reflective value of TiN\textsubscript{x}-SiO\textsubscript{2} coating was similar to