Interference coatings on glass based on photopolymerizable nanomer material

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Abstract

A new sol gel method for the preparation of optical SiO_2 and TiO_2 multilayer coatings has been developed. As an example, a 3 layer antireflective (AR filter) coating and a 5 layer NIR reflective coating on glass are described. For the preparation, a nanoparticulate TiO_2 sol was synthesized by hydrolysis and condensation of tetraisopropylorthotitanate and complex formation with methacrylic acid. A SiO_2 nanoparticulate sol was synthesized analogeously with tetraethoxysilane (TEOS) as the precursor. By mixing both sols in different ratios, layers with tunable refractive index between 1.46 and 2.2 could be obtained on glass after thermal densification at 450°C for 15 min. Three layers (SiO_2 TiO_2, TiO_2, SiO_2) were deposited by dip coating with subsequent UV curing, and the layer stack was thermally densified at 450 C. The so obtained AR filter shows a reflection of $\leq 2\%$ in the wavelength range between 380 and 610 nm, $\leq 1\%$ between 450 and 560 nm and 0% at 550 nm. The AR filter shows very good abrasion resistance and scratch hardness, since only 3% haze is obtained after 1000 cycles of Taber test and the AR filter does not show any damage after 300 cycles of rubber test. The high abrasion resistance can be attributed to the surprisingly low surface roughness (about 6 nm) of the filter. The mechanical and optical properties of the AR filter did not change after sun test with 760 W/m^2 for 320 h and after boiling water test for 11 days.

Keywords: Interference layers; Photopolymerization; Coatings

1. Introduction

Optical systems with defined transmission or reflection characteristics can be realized using interference coatings made by vacuum techniques or the sol-gel-process. Physical vapor deposition and chemical vapor deposition allow the production of interference filters of very high quality, but the investment costs are very high [1]. The sol gel process with SiO_2 and TiO_2 sols is useful for the fabrication of optical coatings with refractive indices between 1.466 and 2.210 on glass after thermal densification at 400°C [2,3]. The sol-gel technique is also a well established industrial process for the preparation of interference filters of large area such as color filter, NIR reflective or antireflective (AR) coatings on glass (shop windows) with sizes up to 3 × 4 m. The coatings consist of 3 to more than 20 layers of different high and low refractive indices (quarterwave layers), and possess good optical characteristics and sufficient stability for many applications [4]. However, the need for thermal treatment at elevated temperatures up to 400°C after every single coating step and the subsequent cooling of the coated glass is costly and time consuming. Alternatively, antireflective coatings are produced as porous SiO_2 single-layers [2 5]. Porosity reduces the refractive index of the layer down to 1.22 [6,7] but also causes loss in stability.

The goal of this work was to avoid the heating step of the glass plate after each quarterwave layer deposition. The approach was to use nanoparticulate coating sols for high (TiO_2) and low (SiO_2) refractive index coatings, which can be fixed to good stability by UV curing before the next layer is deposited, as it has been shown for a 2-layer filter on polycarbonate [10] recently. A stack of several layers should be thermally densified (stack firing) and it was interesting to investigate the optical performance and the stability of the so obtained filters. In order to investigate the application of the stack firing process, a 3-layer AR-system and a 5-layer NIR-reflectance filter were chosen as an example.

2. Experimental

2.1. Sol preparation

The nanoparticulate TiO_2 sol was synthesized by hydrolysis and condensation of tetraisopropylorthotitanate and complex formation with methacrylic acid and a photocata-

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lyst (Irgarcure 156) was added. The nanoparticulate SiO_2 sol was synthesized analogously with tetraethoxysilane (TEOS) as the precursor. Both synthesis routes have been described in detail earlier [10]. For SiO_2/TiO_2-coatings the both sols were mixedin the appropriate ratios.

2.2. Stack fabrication

Coatings were prepared by dip coating on float glass with withdrawal speeds of 3 to 6 mm/s, drying at 25°C for 1 min and fixed by UV-exposure of 2.5 J/cm^2 after each individual coating step. The densification of the AR-filter and the NIR reflectance filter was carried out by thermal treatment at 450°C for 15 min.

2.3. Characterization

Coating thickness, refractive indices and reflection loss were measured by UV-Vis-spectroscopy (Bruins instruments, OMEGA 30) and spectral ellipsometry (SOPRA, ES4G).

The Taber abraser test was carried out with a TABER Industries 5150 Abraser (load 540 g/wheel, rubber CS10F, ASTM D 335978) and the damage of the coating and substrate material was measured with a HAZEGUARD PLUS (BYK Gardner GmbH). The adhesion of the coatings was tested by cross cut tests and tape test [8] and rubber test [9]. In the saline-test, the coated substrates were stored in water containing 0.7 wt.% of NaCl at 100°C for several days. The coated substrates were cleaned with ethanol and a qualitative analysis of the films was performed, every 24 h, with a microscope to detect film delamination or grazing. The sun-test consisted of irradiating the antireflective coated float glass with 760 W/m^2 (simulation of the sun irradiation with Suntest Atlas, xenon lamp without IR filter) and characterized by the determination of the yellowing (Δg) [13] of the coating measured by UV-Vis-spectroscopy.

3. Results

3.1. Design of the AR coating

The characterization of the nanoparticulate coating sols to obtain photopolymerizable thin layers has been described elsewhere [10]. It was be shown that TiO_2 particles with a diameter of 4 nm ($\pm$2 nm) and SiO_2 particles with a diameter of 10 nm ($\pm$3 nm) have been obtained.

The realization of an AR filter with three layers requires three different coatings with high, medium and low refractive index [1]. To adjust the refractive index of the coatings, sols with varying contents of SiO_2- and TiO_2-nanoparticles were prepared by mixing. To determine the refractive indices, the reflection spectrum of appropriate single layers deposited on glass was measured at an incident angle of 7° [10] and compared with results obtained by ellipsometry [11]. Fig. 1 shows the refractive index of the coating after thermal treatment at 450°C for 15 min, depending on the content of TiO_2, obtained with both methods.

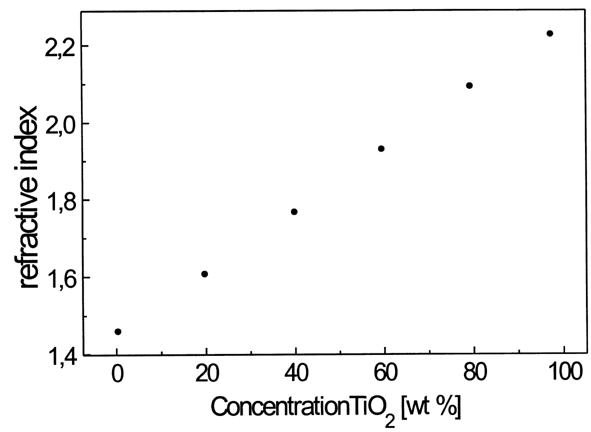

Fig. 1. Calculated refractive index (ellipsometry and reflection spectro scopy) at 550 nm of SiO_2/TiO_2 layers on glass after thermal densification at 450°C, for 15 min. 0% TiO_2 corresponds to a pure SiO_2 layer. The refrac tive index reproducibility of ten samples was $\pm 1.5 \times 10^{3}$.

One can see from Fig. 1 that the refractive index at λ 550 nm increases linearly from 1.46 for 0% TiO_2 up to 2.2 for 98% TiO_2. The deviations for both applied methods are negligible. For each composition ten samples have been prepared and measured. From this, the error of measurement was determined to be $\pm 1.5 \times 10^{3}$.

The design for the 3-layer AR-filter with a minimum of reflection at 550 nm was elaborated by computer simulation (TF calc). As a result, the refractive index (n_D) of the quarterwave layers should be: 1.783 for the first, 2.170 for the second and 1.466 for the third layer.

3.2. Optical properties of the AR filter

After firing this 3-layer stack at 450°C, a highly transparent and defect free filter was obtained, which showed the following reflectance spectrum (Fig. 2).

Fig. 2 shows that the reflection loss is $\leq$2% in the spectral range between 380 and 610 nm and smaller than 1% in the range of 450 to 560 nm. At 500 nm no reflection loss appears. In the range of 450 up to 560 nm, the measured values are smaller than those of the calculated curve (W-filter [1], which is typical for 3-layer antireflective coatings either produced via vacuum technique [12] or sol-gel coatings thermally densified after every single coating step [13,14]. It is assumed that the differences between the measured values and the calculated curve are caused by diffusion processes during the thermal densification step. Before thermal densification the multilayer-stack shows the expected W-filter characteristics [15] and the position of the minima and the maximum of reflection are in very good agreement with the calculated curve. This proves that the stability of the UV cured layers was sufficient for the deposition step, because the stack design was elaborated

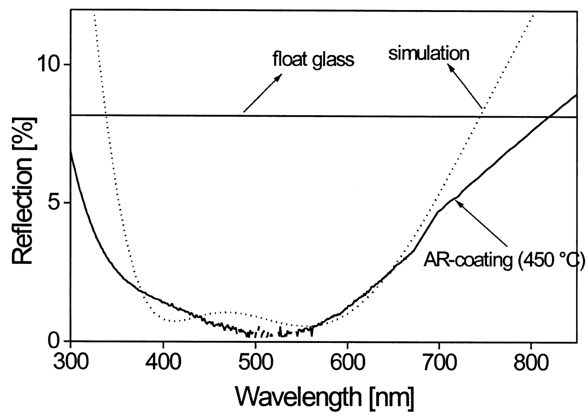

Fig. 2. Reflectance of an antireflective coating on glass (three layers on both sides) before and after stack firing at 450°C for 15 min in comparison with a calculated curve using optical thickness of appropriate single layers fired at 450°C for 15 min.

with single fired layers. During densification, the minimum in reflection loss is shifted to shorter wavelengths.

It is known that layers prepared from sols with high amounts of organosilanes can be densified to glass-like coatings of high optical quality with thicknesses of up to 1 μm [16]. The stack firing of the nanoparticulate layers is new and its basic mechanisms and processes will have to be investigated in the future.

3.3. NIR reflectance filter

In order to see how many layers could be densified by stack firing without damage, a 5-layer NIR reflection filter was prepared using 2 SiO_2 layers of 180 nm in thickness and 3 TiO_2 layers of 125 nm in thickness. The filter could be densified by stack firing without visible defects. The reflectance spectrum is shown in Fig. 3.

As one can see from Fig. 3, 94% reflectance is obtained in the wavelength range between 840 and 1500 nm. The two peaks at about 540 and 760 nm of 30 and 40% reflectance, respectively, lead to slight green color in transmittance. Preliminary experiments show that even seven layer stacks could be fired without visible defects. However further optimization of the stack design will be required to obtain suitable filter characteristics for example for color filter application.

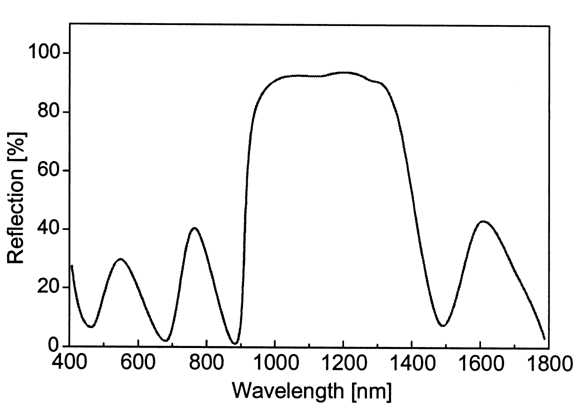

Fig. 3. Reflectance of an NIR reflective filter with 5 layers on each side of a glass sheet after stack firing at 450°C for 15 min.

3.4. Stability tests

It was very interesting to investigate the stability of the fired layer stacks with respect to applications. As a model system, the three layer AR coating was used. In a first step, the abrasion resistance was measured with the standard Taber abraser test. The result of the haze measurements (visible light) as a function of the numbers of cycles is given in Fig. 4.

From Fig. 4 one can see that the uncoated glass shows a haze of about 1.5% after 1000 cycles of Taber test, is in good agreement to reported values in literature [17]. The error of measurement was determined experimentally from five samples each.

For the AR system, a continuous increase of haze is observed and after 1000 cycles a haze of about 2.8% was obtained. From visual inspection it was concluded, that the upper (SiO_2) layer was scratched but was not abraded. The explains, the rather smooth increase in haze with increasing number of Taber cycles. Although further optimization will be required to meet automotive and architectural specifications ((2% haze after 1000 cycles), the measured abrasion resistance appears to be very high. The abrasion resistance is determined by the adhesion and the roughness of the coatings. By cross-cut and tape test excellent adhesion (GT-TT-O [8]) was measured. The surface roughness was determined by atomic force microscopy (AFM). The result is given in Fig. 5.

The nanoparticulate AR stack, shown in Fig. 5 has an average roughness of only 6 nm. In the same range as the particle size (within the error of measurement). This result is surprising and indicates an extremely good arrangement of the nanoparticles during the layer formation. From these

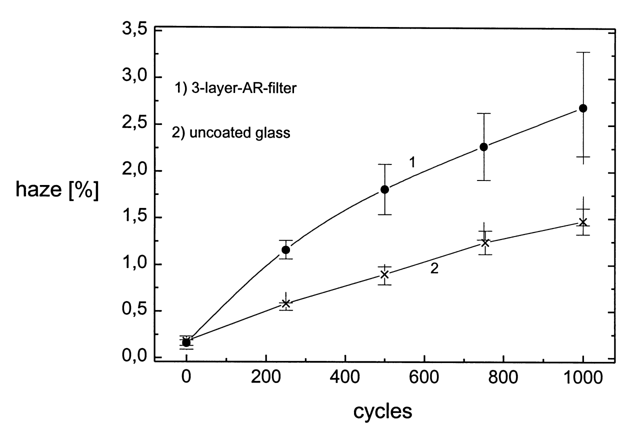

Fig. 4. Haze as function of the number of cycles in Taber abraser test (TABER 5150, load 540 g/wheel, rubber CS10F, ASTM D335978) of the 3 layer AR filter on float glass, prepared by stack firing at 450°C for 15 min in comparison with uncoated float glass.

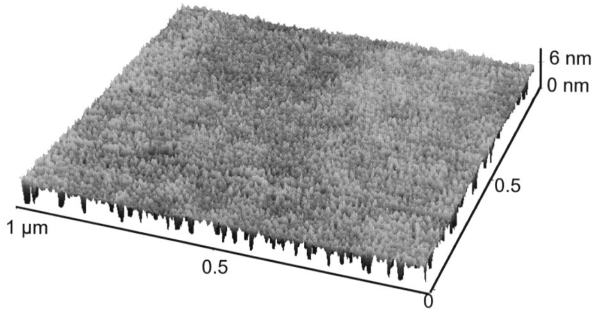

Fig. 5. AFM photography of three layers AR coating on glass after stack firing at 450°C for 15 min.

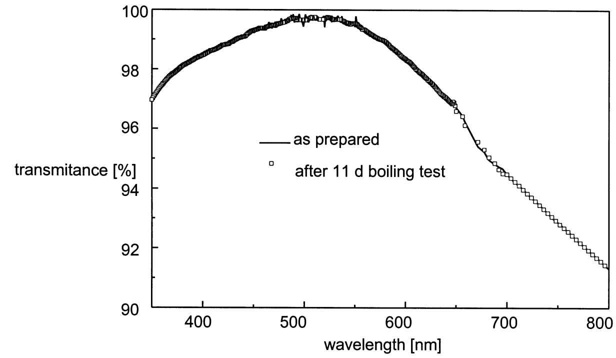

Fig. 6. Transmittance of the AR coating before ( ) and after a 11 days water boiling test (□), according to [15]).

results are attribute the good abrasion resistance of the 3-layer AR stack to the very good adhesion and low surface roughness of the layers.

For further characterization of the coatings, a long term UV-test and a water boiling test (saline test) were performed, according to the standard specifications for optical coatings [9]. After the long term UV test (360 h) no change in the reflectance spectrum shown in Fig. 2 could be detected within the error of measurement. The yellowing Δg [13] was 0% within the error of measurement. For the saline test, samples were exposed to boiling water with 0.7 wt.% NaCl and the coatings were inspected under microscope and the transmittance spectrum measured every 24 h. The result is shown in Fig. 6.

As one can see from Fig. 6, the transmittance is not affected by the water boiling test within the error of measurement. The test was stopped after 11 days (according to [18]) since no delamination or pinhole formation or measurable change in the transmittance spectrum were observed.

4. Conclusion

The use of photopolymerizable nanoparticulate SiO_2 and TiO_2 coating sols allows the preparation of interference filters on glass by stack firing with excellent optical performance, low surface roughness and high durability. This opens up new perspectives for architectural and automotive application, since a sufficient performance and reduced costs can be expected. Future work will focus on the investigation of the interfacial processes during the stack firing and the investigation of the long term stability of the coating sols.

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