Antireflection coating design for plastic optics

Ulrike Schulz, Uwe B. Schallenberg, and Norbert Kaiser

The coating of plastics for optical applications is intended to improve the mechanical durability of soft polymers and to serve an antireflection function. Usually a classic four-layer antireflection system is added on top of a single-layer hard coating. With needle optimization, an alternative coating design has been developed. The design is characterized by thin high-refractive-index layers that are almost evenly distributed over the whole stack. Plasma ion-assisted deposition was used to deposit coatings upon poly(methyl methacrylate), polycarbonate, and cyclo-olefin copolymer. Uniform antireflection and high scratch resistance have been achieved. © 2002 Optical Society of America

OCIS codes: 310.1210, 310.1860.

1. Introduction

Transparent plastics are widely used as optical components. Coating of soft materials is intended mainly to improve the materials mechanical durability. Additionally, an antireflection coating is necessary for many optical applications. Most experience with abrasion-resistant antireflection coatings has been with ophthalmic coatings. In general, coated eye-glasses have to pass severe environmental and abrasion tests to demonstrate their quality. Usually ophthalmic hard coatings are lacquers based on silanols or organically modified silica layers deposited by physical vapor deposition or chemical vapor deposition. An antireflection coating, which consists of four to six single layers as known from classical theory, is arranged typically on top of the hard coating.

For injection molding of optical parts, thermosetting materials such as poly(methyl methacrylate) (PMMA) and polycarbonate (PC) are used. Sometimes only moderate abrasion resistance is required for sensitive handling and cleaning procedures. As we know from our tests, an oxide layer with a thickness of $\geq 1 \mu m$ ensures that conditions for the abrasion test with rubber (International Organization for Standardization standard ISO9211-02-03) required or optical instruments will be met. Nevertheless, the application of thermoplastics as transparent windows for displays will require thicker coatings to fulfill higher demands.

The aim of performing this study has been to develop for plastic substrates a broadband antireflection coating with an average residual reflectance of $\leq 0.4\%$ in the visible spectral range and with a high abrasion resistance. The physical thickness of the coating was to range from 1 to 3.5 $\mu m$. It is well known that the thicker the overall coating, the greater the design possibilities for a desired optical function. Therefore we used a needle optimization procedure to design an antireflection coating by distributing the high-index material in one thick low-index layer instead of the usual combination of a thick hard coating with a thin antireflection coating on top of it. Plasma ion-assisted deposition (IAD) was been applied for deposition of coatings of the new type onto several kinds of plastic. The optical and mechanical properties of coatings have been investigated and compared with those of a four-layer antireflective coating combined with a single silica hard coating.

2. Experiment

We prepared flat samples with optical grade surfaces by injection molding, using a polymer granulate that comprises PMMA 7N (Rhoem), the (PC) Makrolon (Bayer AG, Germany), and the cyclo-olefin copolymer (COC) Topas 5030 (Ticona, Germany).

Uncoated substrates were handled carefully to prevent contamination. We cleaned the substrates before coating them by blowing the samples with ionized nitrogen.

U. Schulz (ulrike.schulz@iof.fhg.de) and N. Kaiser are with the Fraunhofer Institute for Applied Optics and Precision Engineering, Schillerstrasse 1, 07745 Jena, Germany. U. B. Schallenberg is with MSO, Jena Mikroschichtoptik GmbH, Carl-Zeiss-Promenade 10, 07745 Jena, Germany.

Received 27 September 2001; revised manuscript received 3 January 2002.

0003-6935/02/163107-04$15.00/0

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A Leybold APS-904 box coater was used for plasma treatment of substrates and plasma IAD of coatings. During film growth, substrates are bombarded with argon ions emitted by the advanced plasma source, which ensures the formation of dielectric films with high density and stable optical properties.

As a first step in the vacuum process, a different initial treatment for each kind of plastic substrate is useful for good adhesion of evaporated dielectric films. For PC an argon-ion treatment with an advanced plasma source (120 s; ion energy, \( \sim 80 \text{ eV} \)) was applied. PMMA requires a special glow discharge treatment with a dc cathode and an Ar/H\(_2\)O gas mixture to improve adhesion properties. COC can be activated promptly if an ion-assisted layer deposition process is started, and no further treatment is necessary. Initial treatment was followed immediately by electron-beam evaporation of coating materials. Low ion energy (\( \sim 80 \text{ eV} \)) for ion assistance was used for SiO\(_2\) layers to produce coatings with minimal residual stress. The high-index material Ta\(_2\)O\(_5\) was deposited by Ar-ion assistance with an energy of \( \sim 120 \text{ eV} \). Deposition rates were 0.8 and 0.2 nm/s for SiO\(_2\) and Ta\(_2\)O\(_5\), respectively.

The maximum temperature of a substrate during coating was controlled by use of Thermostrip heat-sensor tapes. Spectral transmittance and reflectance of coated samples were measured with a Perkin-Elmer \( \lambda19 \) spectrophotometer. Environmental tests in accordance with the standard ISO9022 and a qualitative steel-wool test were performed.

3. Results and Discussion

A. Design of Hard Antireflection Coatings

For simplification, all calculations presented in this paper were performed with constant refractive indices and normal light incidence with the following values: \( n_L = 1.46 \) for SiO\(_2\) (low-index material, \( L \)), \( n_H = 2.1 \) for Ta\(_2\)O\(_5\) (high-index material, \( H \)), and \( n_s = 1.49 \) for PMMA (plastic substrate).

One common antireflective (AR) layer system is derived from the quarter-half-quarter design

\[
\text{sub/M2HL/air,}
\]

where material \( M \) with an intermediate refractive index was replaced by parts of high- and low-refraction materials. Such a design (AR-4) has the following structure with respect to the physical layer thickness:

Design AR-4 sub/15H24L108H83L/air,

which means, starting from the substrate, 15-nm high-index material, 24-nm low-index material, and so on, with 123-nm Ta\(_2\)O\(_5\) and 107-nm SiO\(_2\) combined. Usually design AR-4 or similar AR designs are adapted to a single hard coat layer for ophthalmic applications.

Our first step in looking for a new design was to reduce the amount of high-index material to make the process for PMMA as cold as possible. Additionally, the low-index part was increased to improve scratch resistance. The needle optimization technique was applied, starting simply with a 1000-nm-thick SiO\(_2\) layer and a target value for residual reflection of 0.4% defined for the spectral range 420–670 nm. The optimization procedure was interrupted after incorporation of four high-index layers. After refinement, a nine-layer-stack (design AR-hard-9; see below for a definition) with a total physical thickness of 1114 nm was achieved:


In Fig. 1 the index profiles and the performance of AR-4 and AR-hard-9 are shown. The high-index-layer thickness of AR-hard-9 is only 47 nm (combined). We found that design AR-hard-9 can be modified to comprise more or fewer layers. \( HL \) layer pairs, where \( H \) is \( \sim 10 \text{ nm} \) and \( L \) is \( \sim 245 \text{ nm} \), have to be added or removed, followed by design refinement. Uneven numbers of layers, from 7 to 35 are at least possible. Typically, the high-index layers are thinner than the low-index layers. We call the antireflective coating AR-hard.

Figure 2 shows some more index profiles and the resultant reflectance. An excellent uniform antireflection effect combined with high scratch resistance can be expected for the thicker AR-hard coatings.

It is obvious that coatings of the type of AR-hard may be regarded as periodic structures. Each period consists of approximately 5–15-nm Ta\(_2\)O\(_5\) and \( \sim 240\)-nm SiO\(_2\). The optical thickness of the periods is \( \sim 3 \lambda/4 \) for a wavelength of nearly 516 nm, which is the reference wavelength for all coatings.

Sometimes the results of needle optimization are not suitable for practical use because of the sensitivity to thickness of very thin layer deposits. It has been estimated that for design type AR-hard the sen-
sitivity of performance to thickness errors in each single $H$ layer is low. If systematic thickness errors of as much as 20% occur, the whole system is shifted slightly to lower or higher wavelength only. The general mechanism of periods of this design type as described is expected to work well even when the calculated thickness of the $H$ layers cannot be accurately achieved in a real manufacturing process. The coating as an arrangement of symmetric three-layer periods $LHL$ will be considered in upcoming research.

B. Antireflective-Hard-9 upon Poly(Methyl Methacrylate)

PMMA is one of the materials for which the coating temperature is critical, because of its low glass-transition temperature of 107°C. No controlled substrate heating was applied during the plasma IAD process, but heat radiation emitted by electron beam guns and an ion source increased the temperature. The thermal load on the substrates depended mainly on the thickness of the Ta$_2$O$_5$ layers because the evaporation temperature of Ta$_2$O$_5$ is higher than that of SiO$_2$. During the deposition of the AR coating AR-4 (which has a high content of Ta$_2$O$_5$) the temperature on the substrate was increased to $\sim$90°C. As a consequence of high thermal stress, film cracking was seen to occur.

Alternatively an AR-hard-9 coating (47 nm Ta$_2$O$_5$ only) was deposited. The maximum temperature on the substrate was raised to $\sim$50°C, and no film cracking was observed. Figure 3 shows transmission measurements of PMMA samples from different batches. The average transmission achieved at 440–670 nm was $\sim$95.5%. The deviations of different batches from this value were low, as expected.

C. Antireflective-Hard-27 upon Polycarbonate and Cyclo-olefin Copolymer

To demonstrate the applicability of the design AR-hard as a hard coating, we deposited a system consisting of 27 layers with a total physical thickness of $\sim$3 $\mu$m upon PC and COC. It had been assumed
that the mechanical properties of a coating are dominated by the properties of silica, because of the low content of high-index material. The mechanical stress of ~250 MPa compressive and the scratch resistance of coating AR-hard-27 were indeed the same as for a single silica layer of 3-μm thickness. Figure 4 demonstrates the result of a steel-wool test of a PC substrate, half of which was coated with AR-hard-27. No damage occurred to the coated area. In contrast, a conventional four-layer antireflection coating (AR-4) upon a plastic substrate was easily damaged by steel wool.

The desired antireflective performance was achieved again without manufacturing problems. Only a quartz-crystal monitoring system was used for thickness control of single layers during electron-beam evaporation. Figure 5 shows measured transmission curves of COC and PC samples with AR-hard-27 coating on both sides. The average transmission achieved from 440 to 670 nm was ~98.5%.

Environmental stability can be an essential criterion of coatings on plastics. In particular, temperature changes are critical for inorganic coatings on plastics because the two have different thermal expansion coefficients. Results of climatic testing show a surprising difference in the behavior of a single silica layer and an AR-hard-27 coating that have the same thickness (Table 1). Thermal stress cracking was observed only for silica coating but not for AR-hard coatings. A relaxation effect of needle layers on the elasticity of the whole coating is therefore assumed.

Table 1. Results of Environmental (ISO 9022) and Adhesion (ISO 9211) Tests of AR-Hard-27 Coating and Single-Layer SiO2 upon COC and PC

<table>
<thead>
<tr>
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<th></th>
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</thead>
<tbody>
<tr>
<td>Tape test snap</td>
<td>No peeling</td>
<td>No peeling</td>
</tr>
<tr>
<td>Heating to 55 °C for 16 h</td>
<td>No defect</td>
<td>No defect</td>
</tr>
<tr>
<td>Heating to 55 °C for 16 h, 90% R.H.</td>
<td>No defect</td>
<td>Film cracking</td>
</tr>
<tr>
<td>Heating to 70 °C for 16 h</td>
<td>No defect</td>
<td>Film cracking</td>
</tr>
<tr>
<td>Heating to 100 °C for 16 h</td>
<td>No defect</td>
<td>Film cracking</td>
</tr>
<tr>
<td>Heating to −25 °C for 16 h</td>
<td>No defect</td>
<td>Film cracking</td>
</tr>
</tbody>
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* Both coatings have a physical thickness of ~3 μm.

4. Conclusion

A new type of antireflection coating has been discussed. In contrast to common antireflection coatings, it consists of a periodic arrangement of thin high-index layers and thicker low-index layers. The periods may have an optical thickness of ~3 λ/4 at the reference wavelength to achieve a broadband antireflective effect. Coatings of the new design type were deposited upon PMMA, COC, and PC by plasma IAD. The hardness of AR-hard coatings corresponds to that of single SiO2 layers of the same thickness. With coatings on both sides of thermoplastic materials, transmission was increased uniformly to more than 98% in the visible spectral range. Low sensitivity of the AR-hard design type to systematic thickness errors of the high-index layers during deposition was observed. The low volume of high-index material inside coatings of the AR-hard type could be interesting also for use in other spectral regions.

References