# Optical Coatings on Polycarbonate for Automotive Applications

*U. Schulz, P. Munzert, C. Präfke, F. Rickelt, and N. Kaiser,*
*Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Jena, Germany*

## ABSTRACT

Transparent thermoplastic Bisphenol-A-polycarbonate (PC) holds an important position as material for optics as well as for automotive glazing. However, the soft and UV sensitive polymer surfaces need to be protected by coatings. For optical applications especially antireflective coatings are inevitable. A comprehensive understanding of complex interactions caused by ultraviolet radiation is a key factor for the development of coating strategies for PC. To protect the interface, optical coatings for PC were realized by incorporating organic absorbers and by exploiting interference effects. In addition, plasma etched nanostructures can be used on the inner surfaces of PC cover glass. The high transparent surfaces exhibit antireflective properties, non-fogging performance and high thermal stability.

## INTRODUCTION

Rigid plastic optical components will replace parts made from glass whenever improved properties or lower costs can be achieved with plastic elements. Coatings for transparent plastics comprise optical interference layers, protective layers, and additional thin films to manage the interface or to provide additional surface properties. At present especially bisphenol-A-polycarbonate (PC) with optical-grade surfaces is used on a large scale for automotive glazing and for covering car instruments. Large transparent surfaces like panoramic roofs, transparent body panels or side/rear windows are becoming increasingly popular in the automotive industry especially to reduce weight [1]. The requirements for coatings on PC comprise an improvement of the scratch resistance and optical characteristics as well as high stability for challenging environmental conditions. PC combines high transparency with high breaking strength and a low weight. However, PC undergoes chemical degradation if exposed to sunlight [2, 3]. Common protection layers are lacquer hardcoats based on acrylic, urethane or siloxane which contain ultraviolet-absorbing molecules [4]. New coating systems for polycarbonate shall provide resistance to more than 10 years of outdoor exposure and a glass-like abrasion performance [5]. For example, the EXATEC-system consists of a UV-lacquer and a scratch resistant layer produced with plasma-enhanced chemical vapor deposition (PECVD) technology [6]. A review the current understanding of the scratch performance of wet-chemical hardcoats and PECVD-based coatings for PC glazing application is given by Seubert et. al. [7]. A challenging requirement for an all-vacuum deposited protective coating is to manage the integration of UV absorbing molecules into the coating [8]. Basic investigations which comprise the thin film formation of several organic compounds and the properties hybrid layers with silica will be discussed in this paper. Polycarbonate is exhibiting a high refractive index (n = 1.67 @ 500 nm) combined with a comparatively low Abbe number of 30. Therefore it is often be used in polymer optical systems to avoid aberration. Optical lenses used in vehicle cameras but also automotive display covers typically need antireflective coatings to reduce the surface reflections. A coating that involves AR properties and scratch resistance has been developed and deposited onto PC by plasma-ion assisted deposition (PIAD). The additional UV-blocking function of the coating was realized by interference effects [9]. A new development incorporates UV-absorbing organic molecules in the vacuum process which can amplify the protection of the interference stack. In addition, for protected areas of polycarbonate such as the inner side of display covers and for optical lenses a new type of antireflective nanostructure will be introduced.

## EXPERIMENTAL

A currently well-established system for the deposition of optical interference coatings on plastics is plasma ion-assisted deposition (PIAD) [10]. All coatings and nanostructures described here were prepared on Leybold APS-904 or Syrus-Pro-1100 coating systems . The coating chamber is typically equipped with an e-beam evaporation arrangement and the advanced plasma source (APS). For evaporation of organic materials a special resistance heating device was used. PC shows various interactions with plasma. According to our experiences plasma pre-treatments were preferably avoided [11]. The ion energy was adjusted in a range between about 80 eV and 120 eV corresponding to an APS-bias voltage range between 80V and 120V. As coating materials for antireflec-

*http://dx.doi.org/10.14332/svc14.proc.1842*

57th Annual Technical Conference Proceedings, Chicago, IL May 3–8, 2014 ISSN 0737-5921

tive function, $SiO_2$ (low refractive index) was alternated with $Ta_2O_5$ or $TiO_2$ (high refractive index). During layer deposition, growing oxide films are bombarded with argon ions emitted from the plasma source. All processes were carried out without substrate heating, and the APS-bias voltage was kept in a low-energy range (80V-100V) to manage the stress behavior [11]. Organic layers and co-evaporated layers were deposited without applying ion assistance.

To produce nanostructures on PC, an initial layer of $TiO_2$ with a thickness of about 5Å to 10Å was deposited by electron beam evaporation immediately prior to etching [12]. The etching was carried out by applying the plasma emitted from the APS. The APS-bias voltage was again kept in a low-energy range (80V-100V) and oxygen was used as the reactive gas. The desired increase in transmission is normally obtained within a few minutes of etching. The PC structure was covered with a 20 nm thick silica layer deposited by electron beam evaporation.

## RESULTS AND DISCUSSION

### Integration of Organic Absorbers Into Vacuum Deposition Processes

A task of research was to develop a combined UV protective and scratch resistant PC coating which can be deposited in a one-step vacuum deposition process. A rough model of the target layer stack is shown in Figure 1. The base layer is a gradient layer which acts as transition zone between the soft polymer substrate and the hard scratch resistant layer. To realize the UV protection of the layer/substrate interface Organic UV-absorbing compounds have to be integrated in this layer. The silica-based top layer shall be deposited in the same vacuum process.

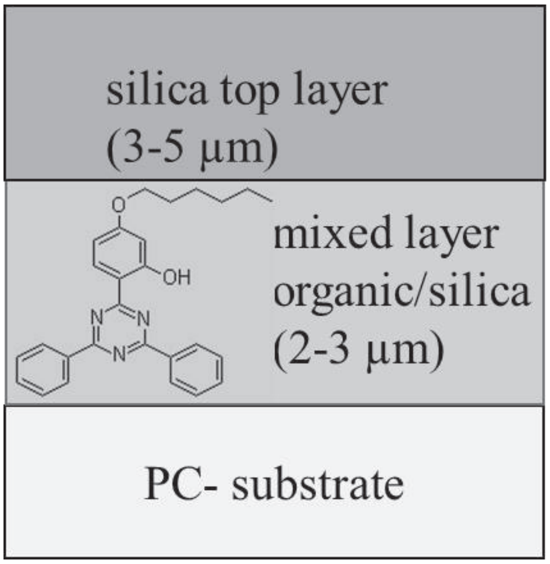

*Figure 1: Schematic of scratch resistant and UV-resistant coating for PC glazing.*

In a first step of research, a UV protective coating containing organic UV-absorbing compounds have been explored. Organic compounds are needed which completely absorb the damaging UV radiation in the wavelength region of 290-400 nm. A suitable absorption behavior were expected by using 2,2´-Methylenebis(6-(2H-benzotriazol-2-yl)-4-1,1,3,3-tetramethylbutyl)phenol (Tinuvin-360) or by 2-(4,6-Diphenyl-1,3,5-triazin-2-yl)-5-hexyloxy-phenyl (Tinivin 1577) [13]. Bothe materials were processed as thin films by vacuum evaporation. In a second step these compounds were thermally co-evaporated with silica. Transparent layers with absorption edges as shown in Figure 2 were obtained from the pure organic materials but also by co-evaporation. However, the chemical interactions between silica and the organic compounds always caused a slight shift and a broadening of the absorption edge. It was found that in case of Tinuvin 1577 the interaction with the silica matrix was less critical for the protection mechanism of the organic molecule compared to other absorbers [14].

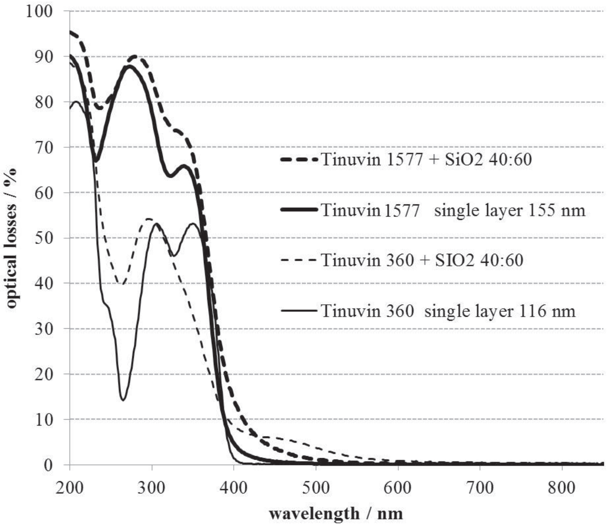

*Figure 2: Optical losses (mainly absorption) of evaporated UV-absorbing layers. The absorption edge of the co-evaporated layers is broadened compared to the single layers.*

Challenging environmental tests with changing climate conditions considering temperature and humidity, as well as simulated global radiation and abrasive media are carried out before such a coating is used on automotive glazing parts. The coatings for roofs have to retain their optical and mechanical properties as well as the layer adhesion for at least 4500 hours of UV irradiation. For comparison, unmodified $SiO_2$ layers show adhesion loss after about 100h. The best mixed layer, a three micron thick co-evaporated layer of silica and Tinuvin 1577, showed still good layer adhesion after 1800h of UV irradiation but failed the automotive standard for roof glazing. Probably, radiation in the visible spectral range together with an insufficient layer thickness is responsible for the adhesion loss after 1800h. New investigations show

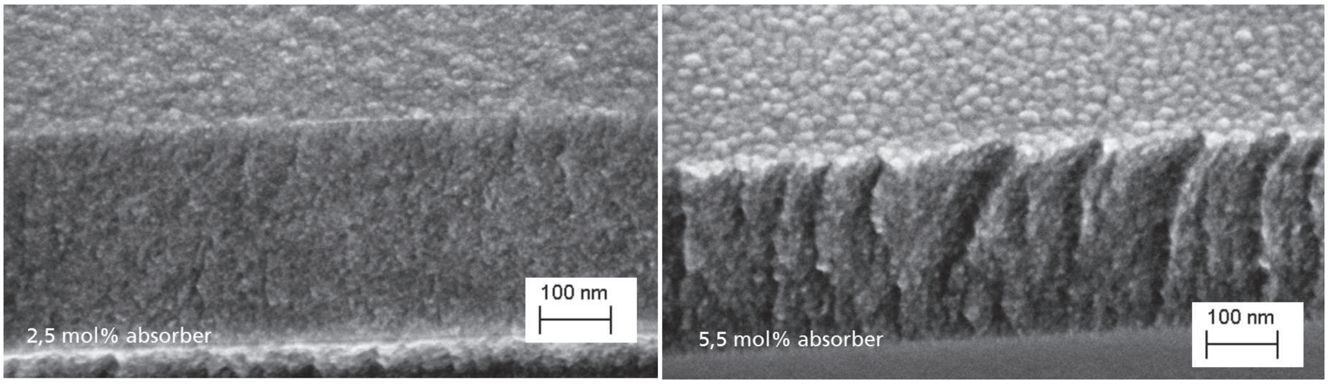

*Figure 3: Scanning electron micrographs of different co-evaporated layers Tinuvin 1577 + silica.*

that also the blue part of visible light is involved in degradation processes of PC [15]. Nevertheless, the transparent co-evaporated layers may be useful for applications of car interior with a lower requirements regarding UV protection. Figure 3 shows scanning electron micrographs of some of the amorphous co-evaporated layers.

### Scratch- Resistant Antireflective Coatings

A common antireflective coating for the visible spectral range (400 nm–700 nm) consists of an arrangement of three to five layers with well-defined refractive indices and thicknesses which provides a reduced reflectance by means of interference effects. The requirements for polycarbonate cover sheets are more challenging. An improved abrasion resistance is desired together with the antireflective property. That can only be realized by depositing a thick coating with more than one micron of total thickness. An additional difficulty for coating polycarbonate is the danger of a later adhesion loss if the coated parts will be exposed to the UV-part of sun light. The requirement for UV-protection for a PC part used inside of the car is 1000h stability in a weathering simulation test.

A special multilayer arrangement has been developed to fulfill these requirements [9]. The chosen layer design consists of 15 layers with a total thickness of 1.5 µm. The UV-problem was alleviated by using a coating with high reflection in the critical spectral range (350 nm–400 nm). The deeper UV-range was blocked by the layer material absorption of titania as high index material. The basic structure of the design follows the AR-hard principle where very thin high index layers are surrounded by thicker low index layers (silica) [16]. Such a “needle” structure helps to limit the stress of the coated plastic part and allows realizing coatings with thickness of up to about 3 microns on PC.

Figure 4 shows the design and the reflectivity measured on a both-side coated PC sheet. The average transmission in the visible spectral range (400 nm-700 nm) was higher than 98 % for normal light incidence. An average reflection of 88 % was obtained in the critical UV-range. The display cover sheets passed the boiling water test and slow temperature change test (-40°C to 80°C) and a 1000 hour global radiation test without film cracking or ablation. For a further improvement of UV resistance an integration of co-evaporated absorbing layers as described in section 3.1 will be developed.

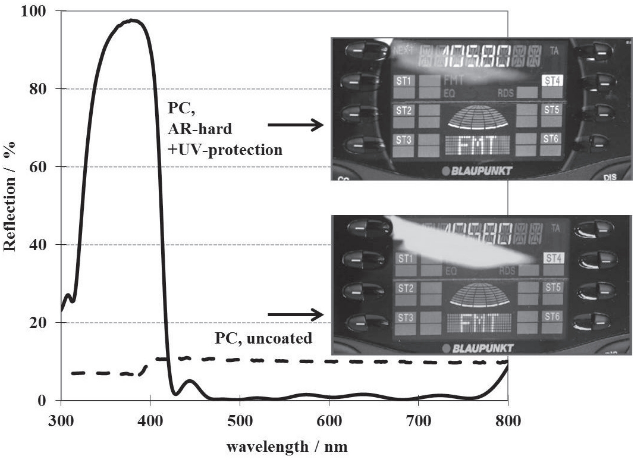

*Figure 4: Reflection spectra of PC with and without AR-coating exhibiting high reflectivity in the UV-A range and low reflectivity in the visible spectral range. The coating was applied to a Blaupunkt™ display cover (both sides coated).*

### Plasma-Etched Antireflective Structures

Stochastically arranged nanostructures can be achieved on many polymer substrates and on organic layers by using the APS ion source for plasma etching [17, 18]. PC undergoes homogeneous material removal when treated with oxygen ions under a $10^{-4}$ mbar pressure range. The etching rate is about 0.8 nm/s. Structure formation occurs if a thin oxide layer is deposited prior to the ion bombardment [18]. Depending on this initial thin oxide layer, the ion energy applied and the etching time, the structure can be modified, resulting in a shift in its reflectance minimum but also in higher or lower scatter losses. Till now an increase of transmission in the range of 3.5 % percent could be achieved. This value is not as good as obtainable for other polymers. However, an enhanced antireflective performance can be expected by lowering the etch time or etching energy for PC but adding in a further step a second organic structure on top of the etched polymer surface as described recently [19].

For common applications in the visible spectral range at normal light incidence, all structures are commonly covered with about 20 nm silica. The hydrophilic silica provides the surface non-fogging properties and improves the environmental and mechanical stability. Figure 5a shows a top-view of plasma-etched PC before covering the surface with silica. The spectral reflectance and the transmission of PC with a single etched AR structure is shown in Figure 5b. In contrast to coatings, etched nanostructures work perfect at elevated temperature. Oxide coatings on polymer substrate normally suffer from the different thermal expansion coefficients of substrate and coating and tend to crack at elevated temperature. PC with AR structure did not show any change of optical properties or of surface morphology during a heat storage test at 115°C for 1000h.

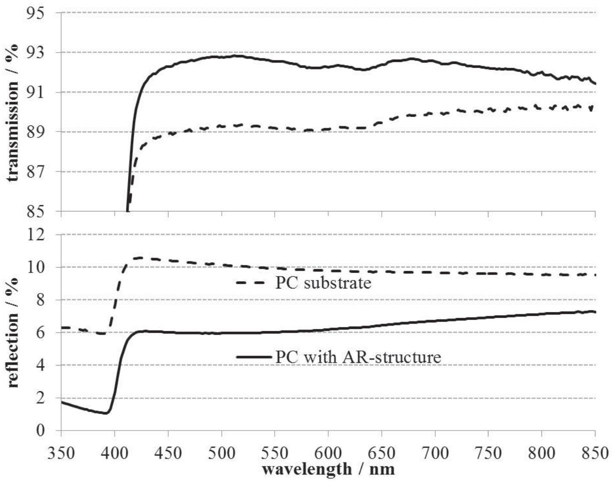

*Figure 5: Spectral reflection and transmission of PC with a single etched AR structure and covered with a silica top-layer (including backside reflection).*

However, the antireflective nanostructures can only be recommended for the inner surfaces of lens systems or cover glass. The structured surfaces are fragile and would be destroyed by cleaning procedures which are required for the outermost surfaces of lenses and displays.

## CONCLUSIONS

The use of PC materials is becoming more and more important for weight reduction and design freedom of automobile parts. Vacuum deposited coatings are desired to improve surface function like scratch resistance and antireflection. However, vacuum deposition of optical and other functional coatings on PC is challenging due to the degradation sensitivity of the polymer. The low-pressure plasma present in modern vacuum processes provides possibilities to activate substrate surfaces, to control the structure of growing layers and to adjust mechanical and thermal film stresses in this way. Comprehensive scientific knowledge is already available to understand the manifold surface plasma interactions especially on PC.

Most important for automotive applications is a combination of antireflective properties with high abrasion resistance and good lifetime properties. The main difficulty for coatings on polycarbonate is the danger of a later adhesion loss if the coated parts will be exposed to the UV-part of sun light. This problem can be overcome by using AR-coatings with high reflection in the critical spectral range or by introducing organic UV-absorbing compounds. As an alternative for interference coatings, etched antireflective nanostructure can potentially provide a better broadband performance for a wide range of light incidence angles.

## ACKNOWLEDGMENT

This work was founded by the German BMBF in the context of the projects “Desiko”, FKZ 03 N3118 F, “Minerva”, FKZ 03 X 3028 E and “EPOS 13 N 12324”, FKZ.

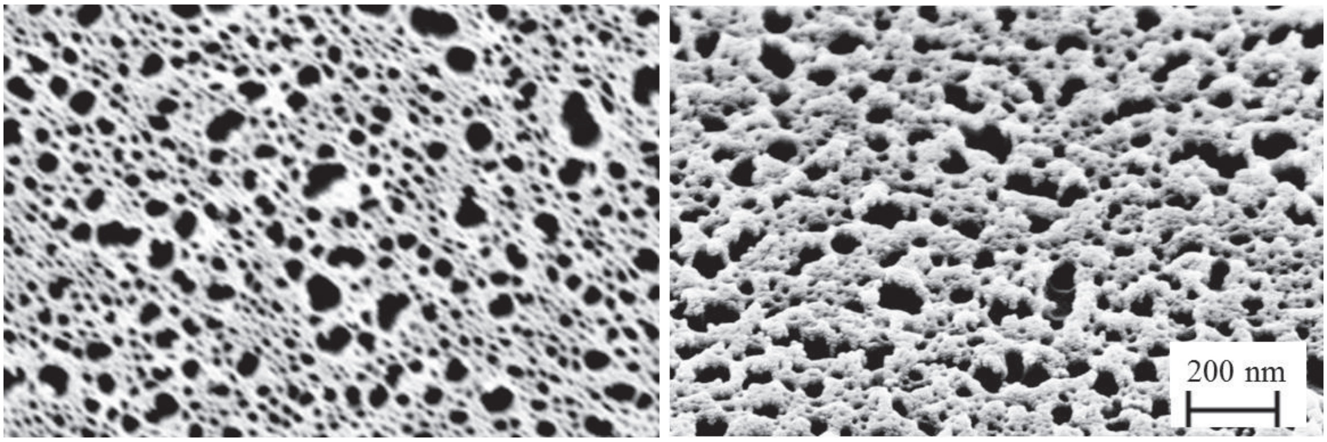

*Figure 6: Top-view of plasma-etched PC before (left) and after (right) covering the surface with 20 nm silica.*

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