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Optical coating and nano-structuring on plastics

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Abstract : 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 optimisation, an alternative coating design has been developed. Plasma ion assisted deposition was used to deposit coatings upon polymers. Uniform antireflection and high scratch resistance have been achieved.

Key words : optical coating; nano-structure; plastic substrate

1 Introduction

Injection moulded or hot-embossed polymer optics will replace glass optics as long as improved properties or lower costs can be achieved with the plastic parts. Highly transparent thermoplastic polymers offer significant weight reduction, cost saving and manufacturing advantages for optical components. Coatings play an important role in this development. Optical interference coatings are required to provide a specific optical function within a desired spectral range. The most common applications are antireflection (AR) coatings to increase the transmitted light or to avoid the formation of "ghost pictures".

An alternative possibility to decrease the reflection on polymer surfaces is the use of appropriate layers with decreasing effective index from substrate site to air. Such layers can be performed by porous sol-gel coatings or by stochastic and periodic surface structures. Periodic sub-wavelength surface structures with antireflection properties were first discovered in nature on the

cornea of night-flying moths and because of that they are called "moth-eye structure"^[1]. The first artificial moth eyes have been produced by the recording, in photoresist, of interference patterns at the intersection of two coherent laser beams^[2]. Today, master structures on a surface area of about 1 m² can be produced in a complex holographic optical process^[3]. This paper presents a new method to produce antireflective surface structures by applying an ion etching procedure onto PMMA^[4].

2 Experimental

2.1 Substrate materials

Some properties of the thermoplastics that are typically used for optics are shown in Tab. 1. Besides several well-known types of Poly-methylmethacrylat (PMMA) and Poly-bisphenol-A-carbonat (Makrolon, Lexan) high transparent Cycloolefin-Polymers (COP, trade names Zeonex or Zeonor) and -copolymers (COC, trade name Topas) enter the optical applications. Cycloolefin polymers are available on

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market for about ten years. They show excellent optical properties and remarkable low water absorption. For applications at higher temperature

polymers like Pleximid, Apec and Ultrason are available.

Tab. 1 Thermoplastic polymers for optical applications

Polymerclass	Types for optics	Manufacturer or sales in Germany	Refractive index at 500 nm	T at 500 nm (%)	HDT (°C)
Polymethylmethacrylat	PMMA 7N, 8N	Roßm GmbH & Co. KG	1.49	92	100
Cycloolefin-polymer	Zeonex E48R, 480R	Zeon Europe GmbH	1.53	91	125
Cycloolefin-copolymer	Topas 5013	Ticona GmbH	1.53	91	125
Poly- n -methylmethacrylimid	Pleximid 8817	Roßm GmbH & Co. KG	1.53	88	166
Polycarbonat-Copolymer	APEC 9351	Bayer Polymers	1.57	90	173
Bisphenol-A-Polycarbonat	Makrolon Al2647, Lexan LS2	Bayer Polymers/ GE Plastics	1.59	90	120
Polyethersulfon	Ultrason E2010	BASF	1.65	80	208

2.2 Coating by plasma-ion assisted deposition

High vacuum Physical and Chemical Vapour Deposition processes (PVD and CVD) are commonly used for the production of optical interference coatings on glass and other inorganic substrates. Vacuum deposition of optical coatings at low substrate temperature is realizable with Plasma Ion Assisted Deposition- technology (Plasma-IAD) using Leybold APS 904^[5]. A thermally evaporated film is bombarded during its growth with energetic ions emitted by the Advanced Plasma Source (APS) as schematically shown in Fig. 1. This results in improved mechanical properties of deposited dielectric films. Applying Plasma-IAD on plastics, the low-pressure plasma can be used in manifold way to modify the polymer surface properties as well as to adjust the mechanical stress of inorganic thin films.

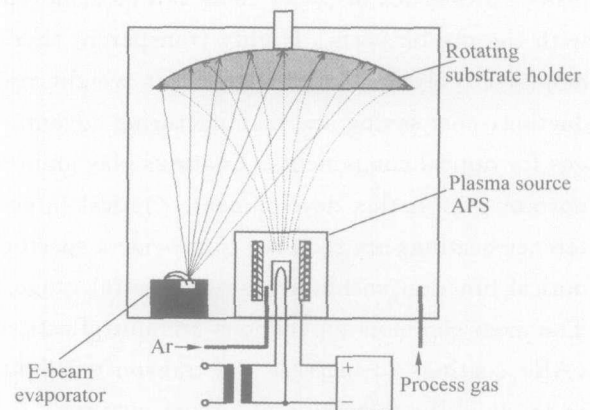


Fig. 1 Plasma-ion assisted deposition using APS904 (Leybold-optics)

3 Results and discussion

3.1 Special processes for different materials

Organic polymers are much more complicated materials for coating than inorganic glasses. The different chemical compositions can lead to varying reactions in contact with plasma or with chemicals^[6-7]. The most significant threat to long-term stability of coated plastics is that

caused by UV radiation or by other environmental factors, which result in slow changes of bulk or interface properties of polymers after coating. High-energy ions and short wavelength radiation emitted by a plasma source have enough energy to break chemical bonds in polymers and thereby to initiate chemical modifications. In summary the following effects have to be taken into account:

- Increase of wettability
- Change of adhesion properties
- Change of refractive index
- Damage of bulk polymer (i. e. yellowing)
- Change of surface topography

In addition, long-term changes concerning most of these effects are possible.

Selected types of PMMA, polycarbonate and poly-cycloolefines have been characterized under coating-relevant conditions like the plasma source APS, UV radiation or the emissions of a running electron beam gun. The surface energy of polycycloolefines and of polycarbonates can obviously be increased by a very short plasma treatment. PMMA is hardly activated and the surface energy rises slowly with APS treatment time. UV radiation emitted throughout plasma ion-assisted deposition processes is able to degrade the optical properties of Zeonex and Topas substrates. PC and PMMA samples irradiated in the same way have not been affected by increasing absorption.

Satisfactory layer adhesion on all plastic substrates exhibit boat-evaporated oxide layers, that can be deposited without the influence of radiation or plasma emissions. Hence, those layers grow on unheated polymer substrate with very low density and show bad mechanical properties therefore. Electron beam gun evaporated oxide layers deposited with plasma ion assistance show the best adhesion on certain types of poly-cycloolefines, polycarbonates, polyamides and polyethersulfones. Especially the poly-cycloolefine polymers ZeonexE48R and Topas5013

and the polyethersulfone Ultrason provide excellent adhesion properties irrespective of pretreatment condition^[8-9]. These materials meet the requirements for the deposition of very thick interference coatings like scratch resistant antireflective coatings, beam splitters or filters. On the other hand, very special process parameters and coating materials have to be used for the ion-assisted deposition of optical coatings on PMMA^[10]. The spectral performance of an AR-coated PMMA sheet produced by a patented process of Fraunhofer IOF is shown in Fig. 2.

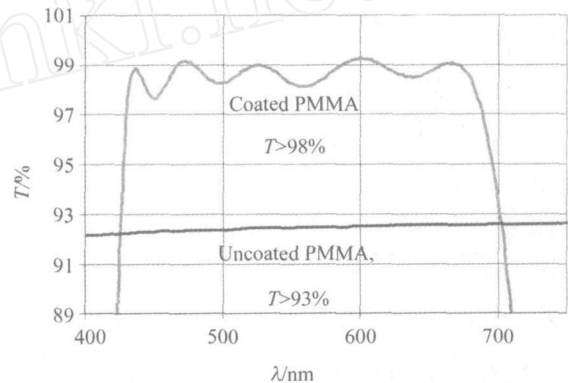


Fig. 2 Transmission of AR-coated PMMA compared to an uncoated sample

3.2 Scratch resistant antireflective coating AR-hard

In general, eyeglasses are subject to physical stresses in practical use and the coated plastic eyeglasses have to pass strong environmental and abrasion tests to demonstrate their suitability. Antireflection layers and hydrophobic topcoatings are typically arranged on top of the hard coating. Alternatively, antireflective coatings AR-hard integrates the antireflection function into a hard layer^[11-12]. The AR-hard coating is scratch resistant itself because of its high overall thickness. Antireflection coatings of the AR-hard type can be understood as an arrangement of symmetrical three-layer periods, each of them consisting of a very thin high refractive index

layer H in the middle of two thick low refractive index layers L. Fig. 3 shows this principle schematically.

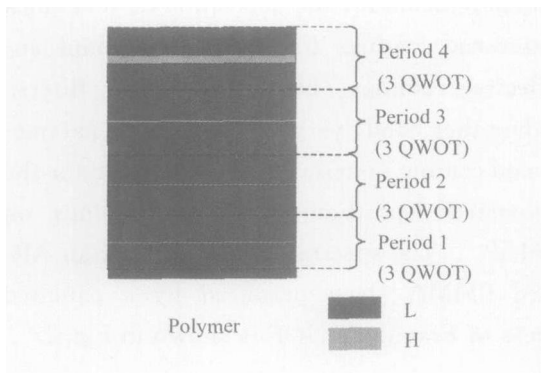


Fig. 3 Schematic of coating design AR-hard ; arrangement of 3-layer periods

Typical layer materials are SiO_2 as a hard oxide with low refractive index and TiO_2 as a high refractive index material. Each of the symmetrical periods can be interpreted as an equivalent layer with three times the Quarter Wave Optical Thickness (3 QWOT) and can be represented mathematically by a single equivalent film having an equivalent index n_{eq} and an equivalent phase thickness. For symmetrical LH periods of three QWOTs the equivalent refractive index can be lower than the index of the low index material L itself used practical for the thin-film combination. The design concept of AR-hard uses such equivalent layers to build up a layer stack with decreasing equivalent refractive index from the substrate side to the outermost surface.

A characteristic value for an AR design is its spectral bandwidth (BW) which is defined by the wavelength at the long wavelength end divided by the wavelength at the low wavelength end. The bandwidth of AR-hard-coatings consisting of three layer LHL periods as described before is limited to about 1.5. This bandwidth covers for example the spectral range of visible light from 450 nm to 670 nm for a target residual reflection of 0.1%. New investigations show that the bandwidth of AR-hard can be broadened if lay-

er stacks with a greater total phase thickness are used in the step-down arrangement instead of the symmetrical layer periods^[13]. As before, each of the layer stacks must meet the condition of mathematical equivalence to a single layer with very low refractive index. Examples for AR-hard coatings with different AR-bandwidth are shown in Fig. 4.

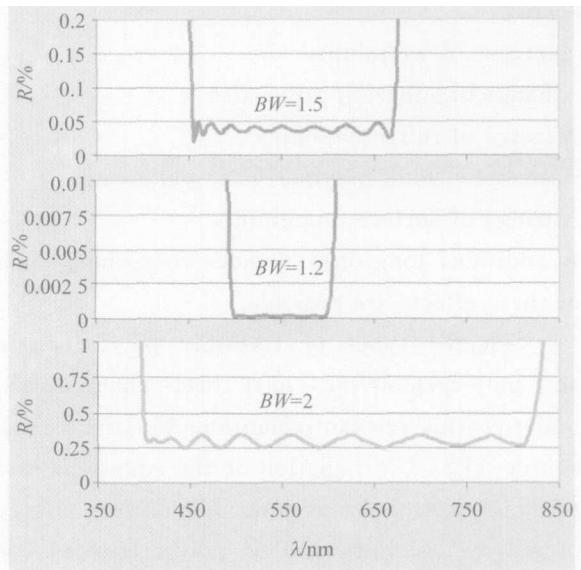


Fig. 4 Residual reflectance of AR-hard coatings with different spectral bandwidths on polymer substrate ($n = 1.53$)

3.3 Generation of the "NANO-moth eye" structure

Low pressure plasma treatment is a convenient way to activate and clean polymer surfaces before coating. Additionally, several ion bombardment processes on polymers are known that initiate etching processes and change the surface topography^[14]. Our investigations show that the application of special ion bombardment conditions leads to stochastic antireflective structures on acrylic surfaces, so-called "NANO-moth eyes". The Advanced Plasma Source (APS) of a Leybold box-coater APS904, which is intended for the production of optical interference layers by means of ion-assisted evaporation was used to perform the etching step. The ion energy, the treatment time and the gas composition deter-

mine essentially the modification of topography as well as the optical properties. The combination of argon and oxygen in the plasma for a treatment time of several hundred seconds leads to excellent antireflective properties on PMMA surfaces.

From a first very fine-grained structure, larger agglomerates are formed with increasing treatment time. These features are almost uniform in size and are stochastically distributed over the surface (Fig. 5). The aspect ratio of diameter and height of the individual features, which should be at least 1:2, is crucial for the antireflection effect without scattering losses.

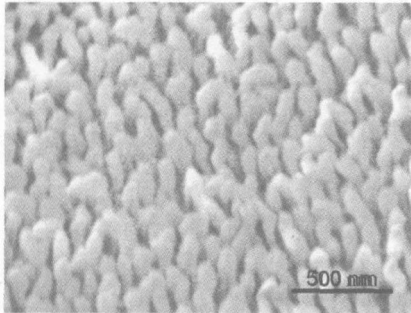


Fig. 5 Scanning electron micrograph of a "NANO-motheye" structure on PMMA

By applying the plasma treatment to both sides of a PMMA sheet, the average reflection can be decreased to less than 1% in a wavelength range from 400 nm to 1000 nm and to less than 0.4% in the visible spectral range of 420 nm to 670 nm. Due to the low scattering losses, the transmission can reach values between 98% and 99% at the same time. Fig. 6 shows the angular dependence of the transmission of a double-sided, plasma-treated PMMA sample.

An antireflective effect has been obtained even at very high angles of light incidence. The stochastic "NANO-motheye" structure remains colourless at oblique light incidence. This behaviour is beneficial compared to periodic antireflection structures.

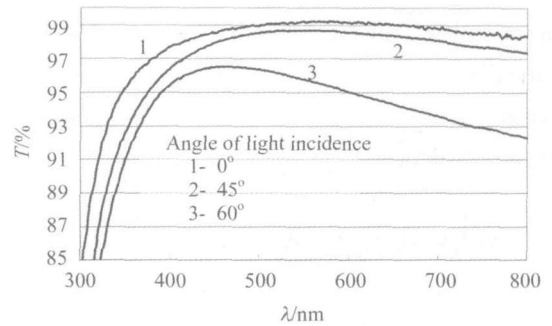


Fig. 6 Transmission of a PMMA sample (plasma-treated on both sides) at different angles of light incidence

4 Summary

The replacement of glass by plastic for optical applications is a challenge for the development of coatings. Coating on plastics requires substrate specific vacuum processes. The suitability of the miscellaneous thermoplastic polymers for vacuum coating processes must be evaluated with respect to the degree of damage these substrates will sustain when in contact with plasma and high-energy radiation. Furthermore, the environmental stability of a plastic part coated with an inorganic layer also depends on the polymer processing parameters and the dimensions of the plastic part. Thus, each coated plastic optic has to pass extended tests depending on the conditions of use. In many cases, the expensive development work impedes the application of coated plastic optics for mass products today. The problems with handling polymers in coating processes stimulate researcher and manufacturer to look for new coating designs or for alternative coating or treatment techniques. One examples of this development is the design concept AR-hard for antireflection purposes. In addition, a new procedure for the production of antireflection structures for plastics using the ion etching process was presented here. A special advantage of the "NANO-motheye" is the attainable high transmission which is independent from surface

geometry. This makes the procedure interesting for complex curved or microstructured components, however the main application is cost-effective moulding and replication, for example by hot embossing.

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Urike Schulz received her Diplom Chemiker in 1986 and her Dr. rer. nat. in 1993 from the University of Jena. After 4 years of research on optical coatings ,she was responsible for the group coatings on polymers at the Fraunhofer Institute of Applied Optics and Precision Engineering in Jena. She has authored a number of papers and patents on processes for polymer coating and coating design. In 2003 she awarded the Josef-von-Fraunhofer-Prize for a new scratch resistant antireflective coating AR-hard .