

Review of modern techniques to generate antireflective properties on thermoplastic polymers

Ulrike Schulz

Modern optical applications need solutions for providing polymer surfaces with antireflective properties. The problems involved in coating comprise thermal limitations, incompatible mechanical properties of coating and substrate materials, and interaction between polymers and plasma. As an alternative for coating, antireflective properties on polymers can also be obtained by hot embossing or by ion etching of surface structures. My objective is to provide the criteria for choosing suitable deposition or structuring methods based on an understanding of plasma-, radiation-, and ion-induced surface phenomena; material compatibility; mechanical and environmental performance; and cost issues. The potential to produce antireflective interference coatings is documented for plasma-enhanced physical- and chemical-vapor-deposition methods, including modern hybrid techniques, as well as for sol-gel wet-chemical processes. The review about state-of-the-art coatings focuses on the thermoplastic acrylic, polycarbonate, and cycloolefin polymers. © 2006 Optical Society of America

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1. Introduction

Injection-molded or hot-embossed polymer optics will replace glass optics whenever improved properties or lower cost can be achieved with plastic parts. The availability of antireflection (AR) coatings or alternative ways to reduce the reflection of polymer surfaces plays an important role in this development. AR properties are required to increase the share of transmitted light, to improve the contrast of displays, and to avoid the formation of ghost images in imaging and illuminating systems. AR coatings have been well established in glass optics for many years, while the coating of polymers is a fast-growing field at present. Applications include plastic eyeglass lenses as well as optical lenses for sensors inside cars, photographic equipment of mobile phones, and a growing number of shields and covers to protect screens and displays.

The formation of AR coatings on plastic substrates is connected with many problems. First of all, the mechanical and thermal properties of polymers differ from those of typical inorganic thin-film materials. Second, a variety of chemical compositions have to be

taken into account on polymer surfaces. Some properties of the most important rigid thermoplastics used for optics are shown in Table 1.^{1,2} The different chemical compositions can lead to various reactions when they come in contact with plasma or with chemicals. The most significant threat to the long-term stability of coated plastics is posed by environmental factors such as UV irradiation and varying humidity conditions, which result in slow changes of bulk or interface properties of polymers after coating. In addition, the permissible temperature for coating processes is limited. This is a difficulty for classical evaporation processes just as for wet-chemical coatings, which require high temperatures for hardening. As a consequence, coating technologies that are well established for glass cannot be used for polymers, and different polymers normally require specialized process parameters.

Only a small number of review articles about coating on plastics deal with the general task.^{3–6} The most extensive experience about abrasion-resistant AR coatings has been gathered in the field of eyeglass coating.^{7–10} Several articles and books specialize on plasma treatments of polymers.^{11–15} The main focus of this paper is on the discussion of procedures and techniques for obtaining AR properties on rigid thermoplastics for optical applications. This concerns dielectric interference coatings and AR surface structures. The most important thermoplastics for optical applications will each be discussed separately,

The author is with the Fraunhofer Institut für Angewandte Optik und Feinmechanik, Albert-Einstein Strasse 7, 07745 Jena, Germany. His e-mail address is schulzul@iof.fhg.de.

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Table 1. Properties of Transparent Thermoplastic Materials^a

Material	Brand Name	n_D (587.6 nm)	Abbc Value V_D	Light Transmittance (%) 3 mm	Tensile Modulus (MPa)	Density (g/cm ³)	Water Absorption (%) 24 h, 23 °C	Deflection Temp. (°C) ASTM D648
Poly(methyl methacrylate)	Plexiglas 7N	1.491	58	92	3200	1.19	0.3	95
Polycarbonate	Makrolon LQ2647	1.585	30	91	2400	1.2	0.12	124
	Apec HT9351	1.566		88	2300	1.15	0.2	173
Polycycloolefin	Topas 5013	1.533	58	92	3100	1.02	<0.01	123
	Zeonex E48R	1.53	56	92	2500	1.01	<0.01	122
	Zeonex 480R	1.525	56	92	2200	1.01	<0.01	123
	Zeonor 1020R	1.53		92	2100	1.01	<0.01	101
	Arton FX4727	1.523	52	92	3000	1.08	0.05	110
	Apel 5014DP	1.543	56	90	3200	1.04	0.09 ^b	125
Polysulfone	Udel P-1700	1.634	23	84	2480	1.24	0.3	174
Polyethersulfon	Ultrason E2010	1.65		80	2700	1.37	2.1 ^c	208
Polyamide	Trogamid CX7323	1.516	45	89	1400	1.02	0.3	122 ^d

^aFrom manufacturers' published data sheets and Refs. 1 and 2.

^bASTM D570 (one week).

^cSaturation at 23 °C.

^dISO75-2 (0.45 MPa load).

including developments in science and technology during the past ten years.

2. Principles for Reducing the Reflection of Polymer Surfaces

A. Interference Layers

The basic theory behind generating AR coatings by using the interference effect has been well known for many years, and approved multilayer designs are available.^{16,17} In principle, there is no difference between the optical performance required for optical parts consisting of a transparent polymer material and that of any inorganic glass. The simplest case for obtaining AR properties on a substrate material with refractive index n_s at a defined wavelength λ_0 is to deposit a thin film with a lower refractive index n and a thickness that is one quarter of that wavelength [quarter-wave (QW) layer]. In theory, a QW layer of magnesium fluoride with $n = 1.38$ may reduce the reflectance of a polycarbonate (PC) surface ($n_s = 1.56$) to $\sim 1\%$ at 500 nm. However, fluoride coatings cannot be recommended for polymers because of their high tensile growth stress and the unsatisfactory mechanical properties of fluoride thin films deposited at a low substrate temperature.¹⁸ The most frequently used broadband AR coatings for the visible spectral range nowadays are adapted from a quarter-half-quarter design and consist of four to six layers.^{19–20} Experience in producing such “classical” broadband AR coatings on polymers exists mainly in the field of eyeglass coating in which the AR layers and hydrophobic top coatings are arranged on top of hard coatings of several micrometers thickness.^{21,7,8,10} Usually, the hard coatings are lacquers based on siloxane. Thus the hard-coated surface, rather than the

more sensitive polymer itself, forms the substrate for vacuum deposition of the AR coating.

The recommendation in applying special optimized AR designs to bare thermoplastics rather than well-applied standard designs developed for glass results from the practical problems with plastic coating. For common thermoplastics, the following requirements should be taken into account for generating AR designs:

- The layer materials and thicknesses have to be adjusted with consideration of the mechanical and thermal film stresses and the heat accumulation during the deposition process.
- The layer materials have to be selected to achieve radiation protection of interfaces or of the bulk polymer, depending on the polymer substrate type.
- The process parameters for the materials used have to be suitable to avoid damage to the polymer bulk and interfaces during thin-film deposition. As a consequence, the refractive index available may be restricted practically.
- The change in the optical properties of interfacial zones due to plasma treatments sometimes has to be taken into account for the design calculation.
- The designs should be suitable for integrating additional functions such as improved scratch resistance, barrier function, antistatic function, or hydrophobic properties.

Modern software design tools are available to generate special broadband AR designs, taking into account the requirements of an individual polymer and its field of application.^{22,23} The design type known under the trade name AR-hard was developed espe-

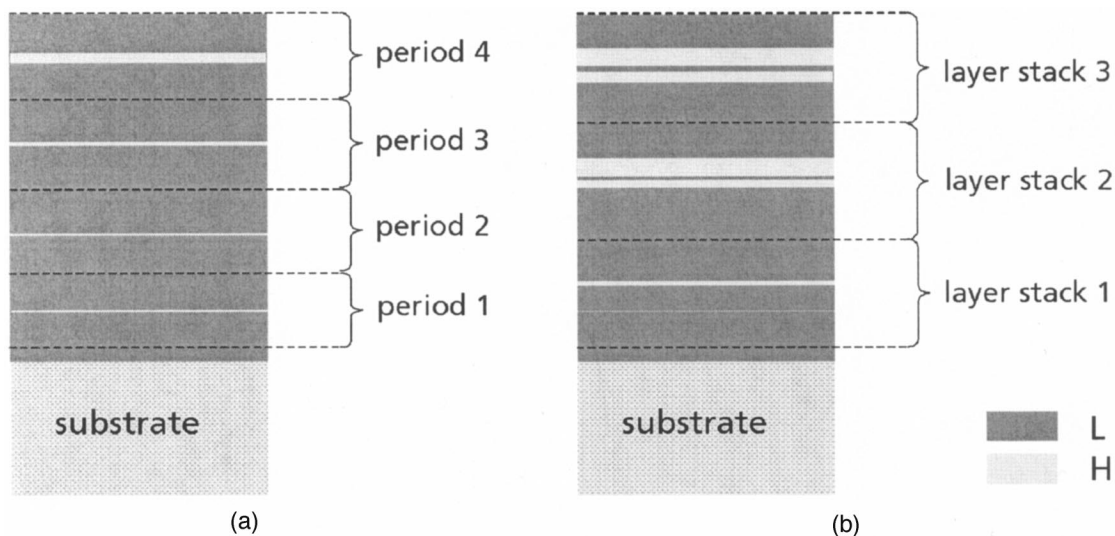


Fig. 1. Schematic illustration of the scratch-resistant AR coating called AR-hard, which is suitable for low-index polymer substrates. Arrangements are of (a) symmetrical periods with 3 QW optical thickness each and (b) nonsymmetrical layer stacks with 4 QW optical thickness. Both arrangements build up step-down designs of equivalent layers: H, high-index material; L, low-index material.

cially for plastic optics to use a higher total thickness for AR coatings with high scratch resistance.^{24,25} The basic idea of AR-hard is to treat symmetrical layer periods as equivalent layers in order to replace layers with practically unobtainable low refractive indices ($1.1 < n < 1.5$). The replacements can be performed by using layer sequences with a total phase thickness of three or more QWs. A basic example is an arrangement of symmetrical three-layer periods, each having three times the QW optical thickness (3 QW). Each period consists of a very thin high-index layer H sandwiched between two thick low-index layers L. Figure 1 shows this principle schematically. The equivalent layers build up a so-called step-down design, matching the refractive index of the substrate to that of the air.²⁶

A remarkable improvement in the performance of broadband AR coatings has been accomplished over the past fifteen years. The designs have changed from the classic quarter-half-quarter design to the so-called multicycle (MC) designs. Cycles²⁷ or clusters²⁸ denote a semiperiodic refractive-index profile previously observed in optimal solutions of broadband AR coatings for particular sets of refractive indices and wavelength ratios. For example, the bandwidth of AR-hard designs can be broadened if layer sequences with greater total phase thickness are used in the step-down arrangement instead of the three-layer periods [schematic shown in Fig. 1(b)].²⁹ Figure 2 shows the residual reflectance available with AR-hard layer stacks for different bandwidths.

B. Inhomogeneous Layers and Surface Structures

Over the past decade, different attempts have been made to produce broadband AR properties that apply single layers in which the refractive index varies gradually from that of the bulk material to unity. The principle is to mix the available low-index material

(e.g., glass or silica) with air on a subwavelength scale. That calls for a compromise between optical and mechanical properties. Layers with decreasing refractive index from the substrate site to air can be achieved by porous coatings or by stochastic and periodic surface structures as schematically shown in Fig. 3.³⁰ To implement AR properties in a certain spectral range by surface structures, one must ensure that the spacing of a suitable array is smaller than the wavelength concerned but that the depth is at least a significant fraction of that wavelength.³¹ Optical properties of such surface structures can be

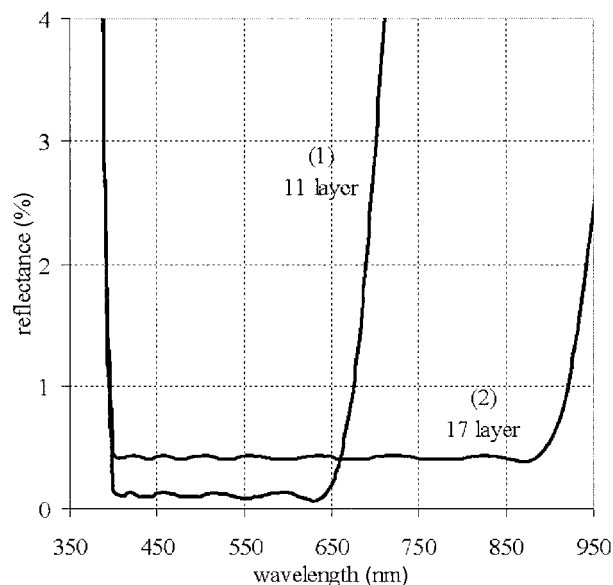


Fig. 2. Performance of AR-hard coatings for different spectral bandwidths, applying basic layer arrangements as shown in Fig. 1(a) (curve 1) and Fig. 1(b) (curve 2). Both examples are calculated for a Zeonex substrate ($n = 1.53$) without a back surface.

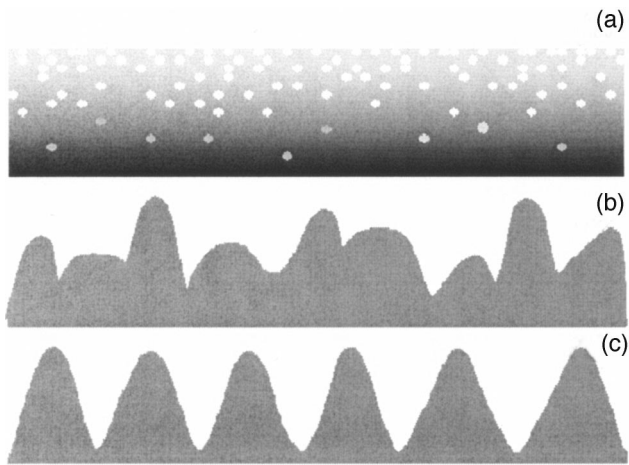


Fig. 3. Schematic illustration of surfaces with decreasing refractive index from the substrate site to air: (a) porous coating, (b) stochastic surface structure, (c) periodic surface structure.

calculated approximately by application of the effective medium theory (EMT). To describe continuous profiles, I separated the gradient layer is separated into homogeneous thin films and regarded as an interference layer.³²

3. Manufacturing Methods

A. Vacuum Coating

Evaporation of oxide materials is still the most commonly used method for manufacturing optical coatings. Naturally, coating on plastics has to be conducted at temperatures below the heat distortion temperature of the plastic. For most thermoplastics this means a temperature limit of $\sim 120^\circ\text{C}$ (Table 1). Only porous coatings would be obtained from thin-film materials evaporated at the low substrate temperature required. During the past decade, important innovations have been established for coating plastics. Present-day coating technologies are based on the application of ion assistance in evaporation processes and the possibility of using cold plasma in chemical-vapor-deposition (CVD) processes.^{33–35,9} As an example of an ion-assisted process, the plasma-ion-assisted deposition (PIAD) technique carried out with an APS 904 coating plant (Leybold Optics) may be mentioned here.⁹ During the PIAD process, the growing film is bombarded with argon ions emitted from the advanced plasma source (APS). The ion energy is in a range between ~ 60 and 180 eV , but for coating plastics only voltages below 120 eV can be recommended. Plasma-assisted evaporation processes for the deposition of AR layers on plastic optics are applied worldwide in industry.^{36,37}

Magnetron sputter deposition is another method of physically depositing inorganic materials. Because of its comparatively high heat and radiation emissions, the sputtering of dielectrics is critical for coating thermoplastics. Nevertheless, some new concepts use the advantage of high precision for the production of AR layers on eyeglasses. Closed-field magnetron sputter-

ing has been described as a flexible low-temperature process suitable for optical coatings on plastics.³⁸ Sputter deposition processes of AR coatings are also applied, following a plasma-enhanced CVD (PECVD) process step that deposits a scratch-resistant layer.^{39,40} Such arrangements may include dc magnetron sputter deposition of silica and titania as well as reactive magnetron sputtering of silica and silicon nitride from a single silicon target. Sputtering is also a basic technology in web coaters for flexible substrates, in which case the undesired heating of the polymers can be prevented by cooling the web over a drum.^{41,42}

CVD is based on the decomposition and chemical reaction of gaseous compounds in vacuum near the substrate surface. One of the reaction products is a solid, which precipitates onto the surface forming a thin film. PECVD techniques used to deposit coatings on plastics use a microwave (MW) or radio frequency (rf) plasma for activating the reacting gases.^{43,44} Because they avoid high temperatures and plasma emissions, pulsed processes will become useful for coating plastics. An innovative plasma deposition process for thermoplastics is provided by the German Schott Hicotec Company.^{45,46} In the plasma-impulsed CVD (PICVD) process, the gaseous precursor is decomposed by a pulsed MW plasma (Fig. 7.4) in Ref. 47. A short ignition of the plasma is repeated many times until the required layer structure has built up. The process is already being used in production for coating light reflectors and eyeglasses. For complex optical multilayers, PECVD processes do not deliver the same thickness accuracy and homogeneity as physical-vapor-deposition (PVD) processes. Moreover, the materials that are suitable as precursors are limited and have to be handled carefully.

B. Wet-Chemical Coating (Solgel Coating)

Wet-chemical coatings can be deposited by dip coating or spin coating on rigid flat or slightly curved substrates. Injection-molded parts of complex forms are not suitable for this deposition method. The solgel process classically involves the use of inorganic salts or metal alkoxides as precursors. Typically, an elevated temperature up to 400°C is needed for hydrolysis and polycondensation to accomplish networking and chemical decomposition until the oxide is formed.⁴⁸ It is essential for coating polymers to avoid high temperatures for curing or using radiation-induced cross-linking reactions for hardening. Typical materials used to improve the abrasion resistance of thermoplastics are organically modified silanes. Silicate-based inorganic-organic hybrid polymers (ORMOCERs) have attracted considerable attention owing to their optical and mechanical properties.⁴⁹ The synthesis entails a chemical modification of organic components to covalently attach them to the inorganic network.

The development of AR coatings using wet-chemical processes comprises mainly single-layer and two-layer systems. Procedures for generating porous layers are baking and burning out the organic particles, which

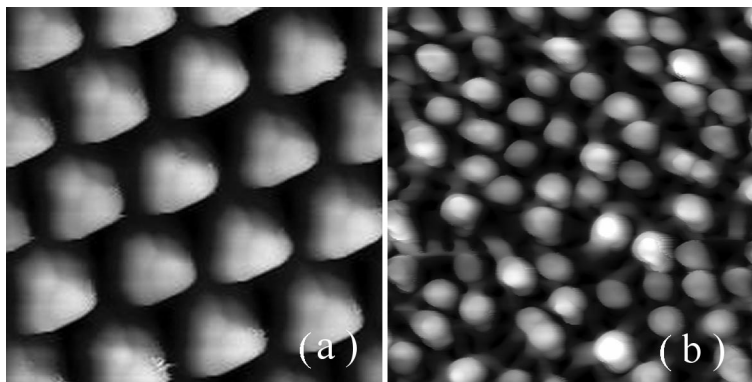


Fig. 4. AFM images ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of AR surface structures on PMMA: (a) hot-embossed periodic structure and (b) stochastic structure produced by direct ion etching.

are in a suspension within a solgel coating,⁵⁰ or the unmixing of a binary polymer blend during spin coating.⁵¹ These processes are described mainly for temperature-stable substrates. The preparation of multilayers by solgel is complex, because the depositing and hardening steps have to be repeated many times. The basic research in this field is focused on the coating material rather than on the kind of polymer substrate or the coating design.⁵² For example, the following AR coatings are results of basic research and are described in the specified references:

- A multilayer for poly(methyl methacrylate) (PMMA) substrates that consists of a hard coating, three-layer AR system and a water-repellent top coating.⁵³
- A four-layer coating for plastics from polymerized nonorganic titanium-containing and silicon-containing solutions. Each layer is cured by thermal treatment before the next layer is applied.⁵⁴
- An alcohol-based inhomogeneous AR layer produced by soaking in acidic or alkaline etchant to dissolve oxide colloids partly from the layer.⁵⁵
- A single composite layer containing organic fluoropolymers.⁵⁶
- A broadband AR and scratch-resistant coating made from tantalum and silicon oxide-based layers. The baking step temperature does not exceed $150\ ^\circ\text{C}$ during 30 min so that various substrates can be coated.⁵⁷
- An interference two-layer AR coating comprising alkoxide or acrylate compounds of Ti, Al, or Zn as the high-index material and hydrolysable organic silicon compounds as the low-index material.⁵⁸
- A two-layer AR coating containing polymerizable nanoparticles modified with alkoxy-silanes and a photoinitiator.⁵⁹
- An antistatic two-layer AR consisting of a solgel alkoxide polymeric material and a colloidal indium tin oxide material.⁶⁰

C. Antireflective Surface Structures

First, periodic subwavelength surface structures with AR properties were observed in nature on the eyes of the night-flying moth.⁶ Artificial AR surface structures

on polymers may have the potential to be inexpensive if they can be replicated by embossing. Initially, technical solutions were generated by using the interference pattern at the intersection of two coherent beams of light from a laser.⁶² Today, master structures for surface areas up to $\sim 0.5\ \text{m}^2$ can be generated in a holographic optical process, and efforts are in progress to increase this area. The outstanding etching behavior of PMMA concerning low-pressure plasma is used to generate a stochastic AR structure directly on the polymer surface.⁶³ All structures described can be transferred to polymer surfaces by hot or cold embossing by using nickel replicas. Figure 4 shows atomic force microscopy (AFM) pictures of AR surface structures generated on PMMA by (a) hot embossing of a periodic moth-eye structure and (b) ion etching. Stochastic structures suitable for AR can also be generated directly on the tool for hot embossing by anodic oxidation of aluminum directly on the tool⁶⁴ or by depositing very rough PVD coatings.⁶⁵ The basic disadvantage of AR structures is their mechanical weakness. The surfaces have to be handled very carefully, and it is practically impossible to clean them. On the other hand, excellent optical properties and cost issues will further promote their industrial application onto protected or build-in optical parts.

4. General Problems for Coating Polymers

A. Interaction between Polymers and Plasma and Effects on Coating Adhesion

Interactions between polymers and plasma; normally cannot be avoided during modern vacuum-coating processes. Please note that emissions from plasma can influence the adhesion of coatings on polymers in different ways. It has been well described in the literature that adhesion is simultaneously related to the complementary effects of roughness, surface energy, surface stabilization reactions, and the possible formation of covalent bonds at the coating-polymer interface. An adhesion improvement by plasma treatments has been variously attributed to improved wettability, to surface cross-linking, or to interfacial diffusion in a depth of typically 5–50 nm.^{66–68} On the other hand, when an adhesive bond breaks at a low

applied stress, the fracture may have occurred exactly at the interface, in a thin layer close to the interface, or as a cohesive fracture in the bulk phase. If poor coating adhesion is observed because of a cohesive fracture in the bulk, the main problem may be the weak boundary polymer layer formed during an unwanted plasma exposure or an applied plasma treatment. In this case efforts should be directed toward strengthening this weak boundary layer rather than to increasing the interfacial attraction.

Electromagnetic radiation at wavelengths below 200 nm has enough energy to break any polymer bond, and for wavelengths below ~ 120 nm the photon energy is sufficient to ionize most organic molecules.⁶⁹ But only radiation that is selectively absorbed by a chosen polymer can initiate chemical effects on that polymer. The penetration depth of the radiation depends on the absorption coefficient and varies between a few nanometers and some millimeters. Important for coating processes are vacuum UV (VUV) radiation at wavelengths below 180 nm. Several investigations show that cross-linking reactions during low-pressure plasma treatments are initiated mainly by VUV radiation.^{70–73}

Modern PVD processes often use ion sources for substrate activation and the densification of growing films. Besides causing radiation effects, the ions typically initiate etching processes that are associated with changes in surface topography⁷⁴ and refractive index.^{75,44}

In addition, interlayers such as nonstoichiometric oxides of chromium and silicon are discussed to improve coating adhesion on polymers.^{76–78} The formation of covalent bonds between atoms of the polymer structure and a metallic atom is the most widely accepted mechanism for high adhesion forces.^{79–80}

B. Mechanical and Thermal Stresses

Residual stresses in thin films are due to the mechanical growth stress of the thin-film material and the thermal mismatch between the film and the substrate when the system is heated during film deposition and cooled from its fabrication temperature to room temperature.^{81–83} As is known from many studies, the mechanical growth stress of thin oxide layers depends mainly on the parameters of the vacuum-deposition process and can be adjusted within a certain range.^{84–86}

Even though many investigations into stress in coatings have been made, less is known about the special case of inorganic coatings on polymer substrates. A different total-stress behavior compared with coatings on inorganic glass has to be considered for oxide coatings deposited on polymer substrates, because of the difference in the thermal expansions of substrate and film, which is the origin of high-level thermal stress. The thermal expansion coefficient of a polymer is typically 1 order of magnitude higher than that for inorganic layers. During PVD and PECVD processes, the substrate temperature is determined as the combination of heat received from the evaporation sources and the plasma sources used in the

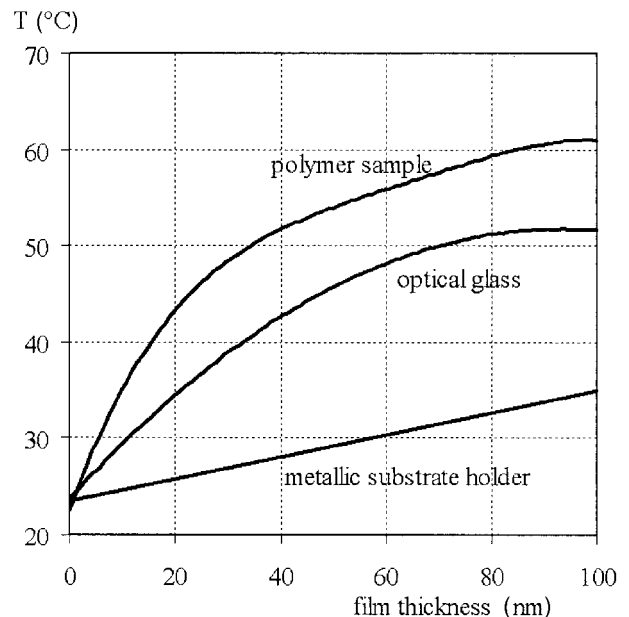


Fig. 5. Temperature development measured *in situ* and simultaneously on a polymer substrate, a glass substrate, and a metallic substrate holder during IAD of a single-layer of TiO_2 .

process.^{87,88} For example, the thermal load on a substrate during PIAD results from both the power of the electron-beam (e-beam) gun and the thermal emission of the ion source. The e-beam power, which depends on the evaporation temperature, melting behavior, and thermal conductivity of the materials, is much higher for most high-index materials than for the low-index SiO_2 . An increase in the maximum temperature on the polymer surface occurs with increasing film thickness at constant ion energy as shown for an e-beam-evaporated TiO_2 layer in Fig. 5. Therefore differences between the stress levels at the coating–polymer interface and on the outer surface have to be expected. It has to be considered in a rough evaluation that a temperature change during the deposition process may generate a stress component of ~ 5 – 20 MPa/K. The stress is tensile during heating and becomes compressive by cooling.⁸⁸ For the complex stress behavior of coatings on polymer substrates to be understood, the temperature has to be controlled carefully during the deposition process. More precise calculations are possible by using complex thermal-stress models that take into account the elasticity theory.^{89–91}

Mechanical coating stress can make it difficult to produce coated plastics that do not show cracking or ablation during their later life. Figure 6 shows a typical stress cracking observed on PMMA coated with $1 \mu\text{m}$ SiO_2 . Although the coatings themselves have compressive growth stress, the stress cracking caused by thermal tensile stress can occur during the deposition of thick layers on polymer substrates. Figure 6(a) shows typical buckling of a coating in the form of “worm tracks” caused by a high compressive growth stress in combination with insufficient coating adhesion. Note that this kind of damage typically occurs if

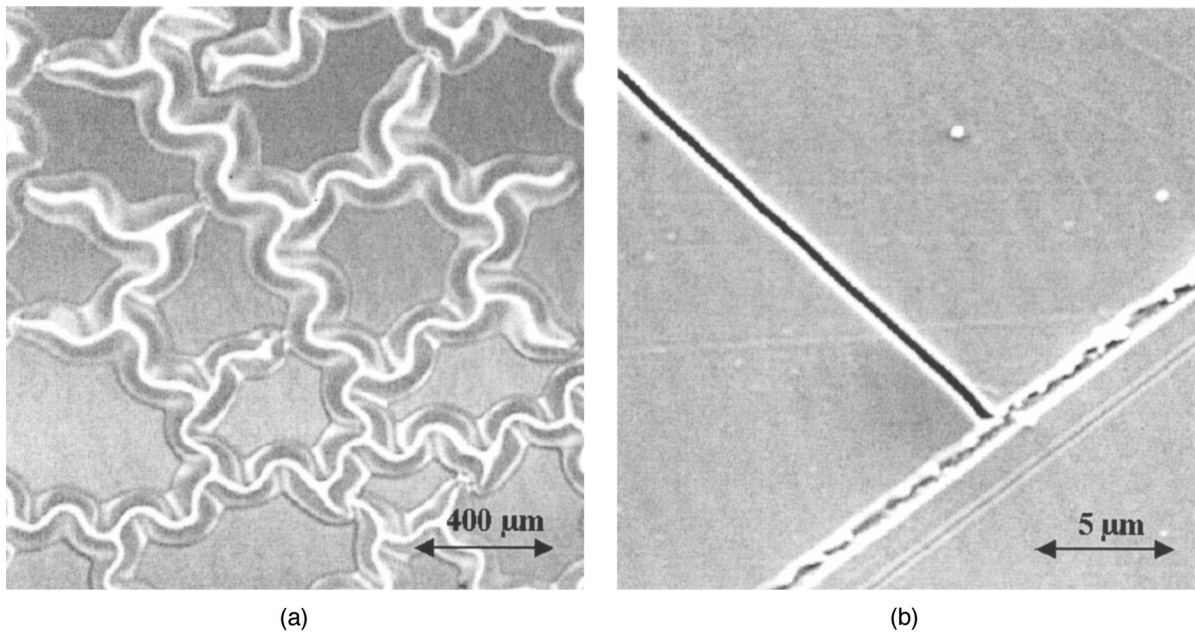


Fig. 6. Cracking behavior of coatings on polymers: (a) buckling of a coating as a consequence of compressive growth stress and insufficient coating adhesion and (b) tensile-stress cracking caused by different thermal expansions of the substrate and coating.

the coating adhesion is low. In Fig. 6(b) the coating has cracked during the deposition process because of high temperature (tensile-stress cracking). The mechanical growth stress of coatings can often be limited by restricting the film thickness and by optimizing the deposition parameters, such as the level of ion energy in the case of IAD,⁸⁵ or by using water vapor as a reactive gas.⁸⁶

5. Experience Gained with Selected Polymer Materials

A. Poly(methyl methacrylate)

PMMA is still the main thermoplastic material used for large lenses such as condensers, Fresnel lenses, and projection TV lenses. Characteristics of PMMA are low birefringence, outstanding hardness, high light-deterioration resistance, and high Abbe number. For vacuum coating, however, this material is problematic. When exposed to VUV radiation, PMMA shows a degradation on its outer surface that depends strongly on the wavelength of irradiation. Photons with energies of ~ 8.5 eV cause the methyl ester group to split off, whereas radiation below this wavelength can break the main polymer chain.^{92,93} Most types of plasma exposure cause weak boundary layers, of decomposition products on the surface that dramatically lessen the adhesion of subsequently evaporated layers. Many different plasma and ion treatments have been investigated for PMMA.^{94–99} Some strong plasma-treatment conditions are capable of removing the ester groups nearly completely and of creating a polyolefinlike surface composition. These treatments have been described to improve the coating adhesion on PMMA.^{100–103,45} The adhesion layers investigated include organic compounds, silicon oxides, as well as thin-metal layers.^{104–107}

Despite the problems, AR coatings on PMMA are available on the market. Suitable technologies are the PICVD process of SCHOTT HiCotec,⁴⁵ the process of NAGASE Company,⁵³ and a plasma-IAD process of Fraunhofer Institut für Angewandte Optik und Feinmechanik (IOF).¹⁰⁸ The latter suggests the deposition of a VUV protective layer without any presence of plasma as the first step in vacuum deposition. After that, a coating of type AR-hard can be deposited by using plasma-assisted e-beam evaporation.

Widely used on PMMA are several types of sub-wavelength AR structures, as indicated in Subsection 3.C. The stochastic AR nanostructure shown in Fig. 4(b) can be generated directly on PMMA by applying ion bombardment in vacuum.⁶³ Figure 7 shows the transmission of a PMMA sample after such a treatment. The low residual reflection remains colorless at normal as well as at oblique angles of light incidence.

B. Bisphenol-A Polycarbonate

Polycarbonate of bisphenol A (PC) (Makrolon, Lexan) is especially important for optical disks and for automobile applications because of its high-impact strength. The characteristics of PC are a high refractive index and a low Abbe number. The disadvantages of the material are high birefringence, low mechanical hardness, and sensitivity to UV radiation. PC is much softer than PMMA and needs a hardening coating several micrometers thick to pass the rubber test according to ISO9211. Various efforts are underway to develop scratch-resistant transparent layers. On automobile parts and eyeglasses, one scratch-resistant sol-gel coating is based on highly filled nanocomposite materials.¹⁰⁹ Protective coatings on PC based on silica and siloxanes [hexamethyldisiloxane (HMDSO) or tetraethoxysilane (TEOS)] can be obtained by applying

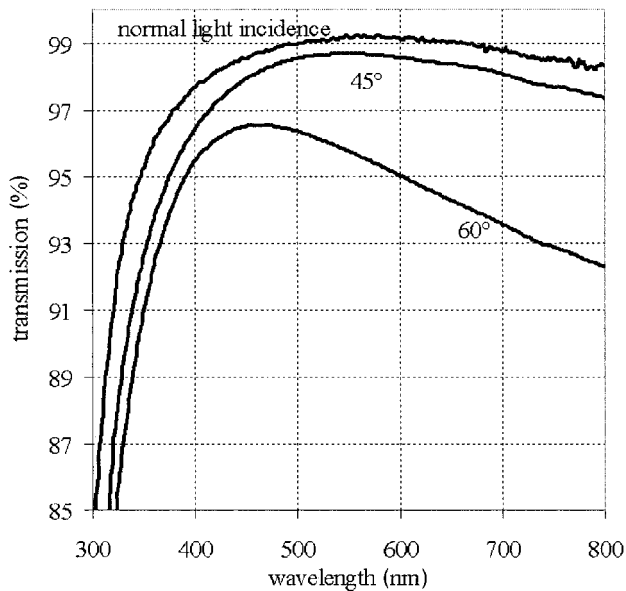


Fig. 7. PMMA with a stochastic AR structure, showing spectral transmission at normal and tilted incidence of light.

different PECVD processes^{110,111} and IAD of silica.¹¹² Different plasma treatments are successfully applied to increase the coating adhesion on polycarbonate.^{113,114} Optical coatings produced by PECVD that consist of SiN_x and SiO_2 are described^{115,116} along with classical oxide layer stacks.²⁵

The degradation of polycarbonate caused by global UV radiation is well investigated, because polycarbonates are prone to yellowing.^{117–119} Most commercially used PC types are protected by stabilizers in the bulk material. It has to be pointed out that the additives do not protect the interfaces from UV-induced degradation. The adhesion of coatings can suffer during a later irradiation of coated parts, unless the coating blocks the radiation at wavelengths below ~ 380 nm. For outdoor applications, coatings on PC have to be provided with UV-protective layers to prevent gradual destruction of the interfaces.

C. Other Polymers

The group of transparent thermoplastics suitable for optical parts comprises certain types of acrylics, polycarbonates, polyamides, polysulfones, polystyrene, and recently cycloolefin polymers (COPs, types of Zeonex, Zeonor, Apel, Arton, and Topas).^{120,121} For most of them, published experience made with regard to their properties for coating did not exist until now. Some results validated for IAD of optical coatings can be presented here from our own experience. For some COPs (Zeonex E480, Zeonex 48R, Topas 5013) coated with scratch-resistant AR layers, high adhesion and outstanding environmental properties have been observed.¹²² COPs show only negligible water absorption and higher thermal stability compared with PMMA. It is estimated that these materials have the potential to replace PMMA particularly for precision optical applications in which thick dielectric coatings

are required. Similarly, recent transparent polyamides (Trogamid CX, Grillamid) can be vacuum coated without adhesion problems. In addition, transparent materials with thermal stabilities up to 180°C have been investigated concerning their properties for vacuum coating, with promising results for the slightly yellow colored polyethersulfone Ultrason.¹²³ The application range of polyamides, as well as of the polyethersulfone, may be restricted by its high water absorption.

6. Summary and Outlook

At present, the development of plastic optics is subject to enormous pressure from applications. Under the conditions of globalization, the time needed to develop a new marketable product becomes incessantly shorter. The introduction of easy-to-form polymer materials becomes important for cost savings in the production of consumer electronics and automobile parts as well as of complex-shaped, high-end precision optical parts.

Up to now, vacuum-coating processes were the most appropriate techniques for producing interference coatings that need a thickness precision in the range of 1 or 2 nm. The use of different low-pressure plasmas to assist the processes has become quite common. Plasma treatments are applied to modify the layer materials in a desired way. At the same time, various interactions with the polymer surfaces have to be taken into account. To minimize the risk and to reduce development costs for the optical parts, one should focus applications that need complex coatings on those polymers that provide the highest process stability. It becomes apparent with optical lenses made from new materials such as Zeonex, rather than from PMMA.

At present, there is a demand for techniques that create AR properties on rigid plastic parts in mass production. Particularly for applications in which glass is to be replaced by plastics to reduce product costs, expensive coating processes are counterproductive. Reactive magnetron sputtering is identified as a possible way to increase the yield of a vacuum-coating process. Sputtering provides an area source that is ideal for scaling processes to any production volume. Also, the hot embossing of “moth eyes” has proved to be highly cost effective, especially for mass production, and may be a suitable alternative to coating procedures. However, the application range of AR structures is limited because the polymer surfaces become soft and soil sensitive. The evaluation of new materials described in patents has demonstrated the potential of solgel techniques for polymer coating. There is an ever-increasing number of new materials that are more compatible with plastic substrates than inorganic materials are. But up to now, manufacturing methods to produce high-precision interference layers by using solgel processes are still uncommon. In conclusion, it is estimated that the requirements of optical technologies will stimulate the industry toward further advancement in process techniques for making AR polymer surfaces.

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