Pattern formation by capillary instabilities in thin films
Morariu, Mihai Dorin

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Chapter 4

Antireflection Coatings
Made by a Sol–Gel Process

4.1 Introduction

Light reflections from computer monitors, car dashboards and TV screens impair the legibility of the displays by degrading the transmission of optical components. The decrease in transmission of a transparent optical medium is caused by the abrupt change in the refractive index at the interface between a medium and its environment. Antireflection (AR) coatings reduce the reflection considerably improving the quality of optical lens systems.

The first ever AR coating was presumably made by Fraunhofer in 1817. He etched glass in a concentrated atmosphere of sulphuric and nitric acid vapors. As a result of the etching process he noted that the reflection was strongly reduced [1]. In 1896 the optical manufacturer D. Taylor stated in an article [2] "... we are very glad to be able to reassure the owner of such a flint (glass) that this film of tarnish generally looked upon with suspicion, is really a very good friend to the (telescope) observer, inasmuch as it increases the transparency of
Figure 4.1: Reflection and refraction of a plane wave. a) When a plane wave of intensity $I$, falls onto a boundary between two homogeneous media of different optical properties, it splits into two waves: a reflected wave $I_R$ and a transmitted one $I_T \approx I - I_R < I$. b) Propagation of light through an AR coated substrate. The reflected light is minimized when the reflected beams from the air–coating and coating–substrate interfaces interfere destructively. In this case $I_T \approx I$.

his objective”. Taylor developed further this chemical etching process to form tarnished films. Today, these are called antireflection coatings. A modern optical system (telescope, microscope or binoculars) would not work without AR coatings. The image would become blurred due to the reflections in the various lenses [3].

In spite of intensive research, the availability of broadband antireflection coatings is still limited by lack of materials with low refractive indices. The work presented in this chapter describes a new method of producing nanoporous hard AR coatings with improved optical transmission.

### 4.2 Principle of AR Coatings

The reflection loss of an optical surface is related to the difference between the refractive indices of environment and the optical material. The theory explaining the optical behavior of single and multiple homogeneous coatings
is well understood \[4, 5\]. For good antireflection properties, a coating must satisfy two conditions that lead to complete destructive interference (Fig. 4.1):

1. **The Phase Condition:** For the destructive interference of the reflected beams, the length of the optical path in the layer has to be equal to one half of the light wavelength. This quarter–wave condition gives the ideal thickness of the coating:

\[
\lambda_0 = 4n_c \cdot h_c
\]

where \(\lambda_0\) is the wavelength at which destructive interference occurs.

2. **The amplitude condition:** For complete destructive interference, the amplitudes of light reflected from the coating–air and substrate–coating interfaces have to be equal. This condition is satisfied when the refractive indexes of the coating \((n_c)\), the environment \((n_e)\) and the substrate \((n_s)\) are given by the following relation:

\[
n_c = \sqrt{n_e n_s}
\]

If air is the environment \((n_e = 1)\) then \(n_c = \sqrt{n_s}\).

The reflection from a coated surface is given by Fresnel’s equation

\[
R_m = \left(\frac{n_c^2 - n_e n_s}{n_c^2 + n_e n_s}\right)^2
\]

When the surface is coated with a film of refractive index \((n_c)\) that varies continuously from \(n_s\) to unity and thickness larger than the reference wavelength, zero reflectance is obtained for the reference wavelength. The principle of inhomogeneous AR coatings is depicted in Fig.(4.2). There are two approaches to produce graded refractive index coatings. One is to pattern the substrate surface with a subwavelength periodic structure (Fig. 4.2a) and the second is to use a nanoporous coating (Fig. 4.2b).

The two approaches differ only in the smooth variation of the optical constants throughout the thickness. In the first case (Fig. 4.2a), the refractive index of the inhomogeneous layer decreases gradually from \(n_s\) to unity. Therefore, to produce such a coating, a material with the same refractive index as
Figure 4.2: Two approaches of using inhomogeneous layers as antireflection coatings. a) The “moth–eye” type of AR coating introduces a smooth transition between the optical properties of environment and substrate. b) The nanoporous type of AR coating. The refractive index of the coating depends by its porosity and is the average between the refractive index of the pores and the matrix.

The substrate has to be used. The optical properties of such a sub–wavelength structured surface are explained by considering that the surface structure acts as a periodic diffraction grating. If the period of the grating ($\lambda_{\text{structure}}$) is small compared to the wavelength of light, only the zero–order diffracted wave propagates and higher diffraction orders are suppressed \[6, 7\]. However, with increasing the angle of incidence, it is more difficult to avoid higher–order diffracted waves propagating into the substrate.

The optical properties of the nanoporous layer (Fig. 4.2b) can be described using a different model \[8, 9, 10\]. The refractive index of a material is related to its density. By introducing porosity, the material density decreases, resulting in a smaller refractive index. To prevent scattering two conditions have to be met: the pore sizes have to be much smaller than the wavelength of light and the pore distribution has to be homogeneous. The relation between the density and the refractive index of such porous materials is \[8\]

$$\frac{n_p^2 - 1}{n_c^2 - 1} = \frac{d_p}{d_c}$$  \hspace{1cm} (4.4)

where $n_p$ and $d_p$ are the refractive index and the density of the porous material and $n_c$ and $d_c$ are the refractive index and the density of the solid material.
4.3 Experimental method

Eqn. (4.4) is written in terms of porosity as

\[ \frac{n_p^2 - 1}{n_c^2 - 1} = 1 - \frac{P}{100} \]  

(4.5)

or

\[ n_p^2 = (n_c^2 - 1) \left( 1 - \frac{P}{100} \right) + 1 \]  

(4.6)

where \( P \) is the percentage of porosity. When \( P = 0 \% \) (no pores), \( n_p = n_c \). When \( P = 100 \% \) (no solid material), \( n_p = 1 \).

4.3 Experimental method

The refractive indices of glass and transparent plastic substrates are typically \( n_s \approx 1.5 \). From Eqn. (4.2), the optimal refractive index for a single–layer broad–band AR coating is

\[ n_f = \sqrt{n_s} \approx 1.22 \]

The lowest refractive indices for dielectrics are on the order of 1.35 (\( CaF_2, MgF_2 \)). A value of \( n_f = 1.22 \) is therefore unreachable for conventional single layer AR coatings.

Instead of a homogeneous layer, Walheim et al. [11] used a nanoporous film. When the pore size is much smaller than the visible wavelengths, the effective refractive index of the nanoporous medium is given by Eqn. (4.6). To lower the refractive index to \( \sim 1.23 \) using a material with a refractive index of \( \sim 1.5 \), a porosity of \( \sim 60 \% \) has to be introduced. The technique used by Walheim et al. was based on the demixing of a binary polymer blend during spin–coating. The process is schematically described in Fig. (4.3). Standard polymers such as polystyrene and poly(methyl methacrylate) and solvents were used.

During the phase separation process, one of the polymer components forms domains in the matrix of the other. The development of the lateral phase morphology depends strongly on several preparation parameters. Immediately after deposition (Fig. 4.3c), the film appeared transparent and featureless due to similar values of the refractive index of polymers and substrates. To create a porous film, one of the two polymers was removed by exposing the film to a selective solvent (Fig. 4.3e). Two cases were distinguished:
Figure 4.3: Preparation of a nanoporous coating. a) The solution consisting of two polymers in a common solvent is placed onto the substrate. During spin–coating b), phase separation sets in, and after evaporation of the solvent a lateral phase morphology is obtained c). The film is exposed to a solvent e) that is selective for one of the polymers, producing a porous film f).

i) if the pore sizes were comparable to the light wavelength, the coating appeared opaque. The phenomenon is due to light scattering by the pores.

ii) when the pore sizes were much smaller than all optical wavelengths, the film remained transparent.

The obtained nanoporous film had remarkable antireflection properties, strongly reducing the amount of reflected light.

A limitation for the applicability of this simple and elegant method on industrial scale was the lack of wear resistance of the polymer–based AR layers. To overcome this disadvantage, we developed a new method based on a sol–gel approach. This method allowed us to produce high–quality, broadband AR coatings with improved mechanical properties. Applying our concept
to organic–inorganic hybrid materials enabled us to replicate the nanoporous polymer films into silica mineralized AR coatings. The new sol–gel derived nanoporous silica films had broad–band antireflective properties.

4.3.1 Novel Routes for the Preparation of Mineralized AR Coatings.

We developed two methods for obtaining porous sol–gel coatings. Both techniques produced broad–band, high–quality AR coatings.

**Water Based Process to Manufacture AR Coatings**

This experimental procedure is based on water soluble components, therefore being a 100 % environmental friendly technique. We produced a SiO$_x$ solid network starting with the precursor ”Natron Water Glass” (Na$_2$Si$_3$O$_7$). The structure of the SiO$_x$ network was formed by controlling the condensation of small primary silica particles (polymeric or colloidal) with a diameter of a few nanometers.

These particles are dispersed in a liquid, forming a so–called sol. Increasing the particle number and sizes increases the density of the sol. Eventually, the particles start to touch each–other, forming a sponge–like three–dimensional network, called gel.

In our approach we stopped the process in the sol state. This way, we were able to spin–coat the solution. To form the sol, acetic acid was added to an aqueous solution of sodium silicate (water glass):

$$\text{Na}_2\text{SiO}_3 + \text{CH}_3\text{COOH} \xrightarrow{\text{H}_2\text{O}} [\text{SiO}_2 \times (n) \text{ H}_2\text{O}] + 2\text{Na}^+\text{COOH}^- \quad (4.7)$$

The chemical reactions during the sol–gel process are described by three equations [12]:

$$-\text{Si} - \text{OR} + \text{H}_2\text{O} \xrightarrow{\text{acid or base}} -\text{Si} - \text{OH} + \text{ROH}$$

$$-\text{Si} - \text{OH} + \text{HO} - \text{Si} - \rightarrow -\text{Si} - \text{O} - \text{Si} + \text{H}_2\text{O} \quad (4.8)$$

$$-\text{Si} - \text{OR} + \text{HO} - \text{Si} - \rightarrow -\text{Si} - \text{O} - \text{Si} + \text{ROH}$$

The first equation in Eqns.(4.8) defines the hydrolysis process, while the other two define the condensation process. Both processes are strongly influenced by
the concentration of the components, the nature of solvent, the temperature and the pH of the solution. In our method, due to the acidic conditions (pH: 2–5) hydrolysis was favored. A large number of monomers and small oligomers with reactive Si–OH groups were formed. These molecules reacted with each other forming the sol solution.

Adding an organic polymer to the sol solution, resulted in a phase separation between the inorganic and the organic phases when evaporating the solvent. The subsequent removal of the organic phase resulted in a porous silica film. We were able to obtain a pore size of $\sim 50$ nm in diameter by varying the amount of the polymer and the sol particles.

Our method consisted of 4 steps:

**Step1: Preparing the solution.** Solutions of 10\% $\text{Na}_2\text{Si}_3\text{O}_7$ and 10\% polyacrylamide (PAA) (by weight) in water, were made. Subsequently, the solutions were mixed in a weight ratio of 5:1.

**Step2: Adding the acid.** 40 $\mu$l of acetic acid ($\text{CH}_3\text{COOH}$) was added to the solution. The mixture was stirred for $\sim 20$ seconds at room temperature.

**Step3: Coating the substrate.** White glass slides with a refractive index of $\approx 1.5$ were coated on both sides by spin–coating at 5000 RPM.

**Step4: Removing the organic component.** The PAA polymer was removed by washing the sample in water for $\approx 60$ seconds. A longer washing time did not produce samples with different spectral properties. The sample was subsequently dried at room temperature in a nitrogen jet.

**AR coatings prepared from TMOS precursors.**

A second method to prepare hard AR coatings made use of tetramethoxysilane $\text{Si(OCH}_3)_4$ alkoxide as precursor and poly(methyl methacrylate) (PMMA) as organic component. We prepared the sol phase by polymerizing tetramethoxysilane (TMOS) monomers in an acidic environment, using hydrochloric acid (HCl) as catalyst. Hydrolysis and polycondensation reactions occured when water and catalyst were added to the precursor $[12, 13, 14, 15, 16, 17, 18]$. The hydrolysis reaction is:

$$\text{Si(OCH}_3)_4 + \text{H}_2\text{O} \xrightarrow{\text{HCl}} [\text{SiO}_2 \cdot \text{H}_2\text{O}/\text{CH}_3\text{OH}] \quad (4.9)$$
4.3 Experimental method

The condensation reactions are:

(alcoxolation)

\[(\text{OCH}_3)_3\text{Si}–\text{OH} + \text{HO}–\text{Si}–(\text{OCH}_3)_3 \rightarrow (\text{CH}_3\text{O})_3\text{Si}–\text{O}–\text{Si}–(\text{OCH}_3)_3 + \text{CH}_3\text{OH}\]

(oxolation)

\[(\text{CH}_3\text{O})_3\text{Si}–\text{OH} + \text{HO}–\text{Si}–(\text{OCH}_3)_3 \rightarrow (\text{CH}_3\text{O})_{x-1}\text{Si}–\text{O}–\text{Si}–(\text{OCH}_3)_3 + \text{H}_2\text{O}\]

The two chemical processes take place simultaneously in the sol–gel process. The sol solution was subsequently mixed with a PMMA solution and spin–coated onto the substrate. After removing the PMMA, a porous layer with high–quality AR properties was obtained. The three step method of preparing the coating is:

**Step1: Preparing the solution.** The TMOS precursor was mixed with a diluted hydrochloric acid solution in a weight ratio of 6:2.3. The diluted HCl solution was obtained by mixing 0.02 ml of hydrochloric acid (fuming) with 10 ml deionized water. Tetrahydrofuran (THF) was added to the aqueous TMOS solution in a weight ratio of 3:1. This solution was subsequently mixed in a weight ratio of 1:1 with a 3% solution of PMMA in THF. The final solution was diluted 1:1 by weight with THF.

**Step2: Coating the substrate.** White glass slides with a refractive index of \(\approx 1.5\) were coated both sides by spin–coating at 2000 RPM.

**Step3: Removing the organic component.** The PMMA was removed by washing the sample in acetone for \(\approx 60\) seconds. A longer washing time did not produce samples with different spectral properties. The sample was subsequently dried at room temperature in a nitrogen jet.

For both Na\textsubscript{2}Si\textsubscript{3}O\textsubscript{7} and TMOS based preparation methods, the resulting porous silica layers (Fig. 4.3F) increased the optical transmission through the glass substrates in the visible wavelength range to \(T \approx 99\%\). For the reference wavelength of \(\lambda = 600\) nm, a transmission of \(\approx 99.8\%\) was achieved. We adjusted the thickness of the layer by varying the rotation speed in the coating process. The optical transmission spectra of a glass slide coated on both sides with a 120 nm porous silica coating is shown in Fig.(4.3.1) (circles). By increasing or decreasing the thickness, the maximum of the transmission
Figure 4.4: Transmission curve of a glass slide coated on both sides with a 72 nm (black hexagons), 120 nm (open circles) and 170 nm triangles thick porous silica layer. The solid curve is the theoretical fit to the experimental data (open circles) yielding a refractive index $n_c = 1.289 \pm 0.05$. The inset show for comparison the transmission curves of an uncoated (squares) and MgF$_2$ coated (circles) glass slide.

The advantage of the TMOS based technique compared to the Na$_2$Si$_3$O$_7$ coating is a better applicability on an industrial scale. The Na$_2$Si$_3$O$_7$ coating solution in water was very unstable due to the short time needed for gelation process to take place. The sol solution turned into a gel in less than 30
4.3 Experimental method

seconds, leaving only little time for spin–coating. However, the reaction could be somewhat stabilized by changing the amount and the nature of the acid. In comparison, the TMOS based coating solution was stable for $\sim 3$ hours at room temperature. At lower temperatures ($\sim 4^\circ C$) the stability of the solution increased to 3–4 days.

Porous films were obtained by the subsequent removal of the inorganic phase. In Fig.(4.5), Tapping–AFM and SEM images of the nanoporous layers are shown. In the case of AFM imaging, the resolution is limited by the radius of the tip curvature. The images are therefore a convolution of the surface topography with the tip shape. This tip artefact is visible in Fig.(4.5a). SEM images helped to visualize the unconvoluted pores (Fig. 4.5b) and the cross-sectional SEM micrographs (Fig. 4.6) revealed a homogeneous distribution of the pores inside the coating.

4.3.2 AR Coatings on Plastic Substrates

The substrates used in Section 4.3 were white glass slides with a refractive index of $\approx 1.5$ ($\lambda=532 \text{ nm}$). However, plastics have become important materials during the past decades, due to their high processability, light weight and low cost. They are used for ophthalmic lenses, sunglasses, displays, etc. Poly(methyl methacrylate) (PMMA) and poly(carbonate) (PC) are some of
the most common polymers used for optical applications on an industrial scale. The progress in vacuum technology and the development of high yield sputtering systems made it possible to deposit metal and dielectric layers onto plastic substrates [19, 20, 21, 22]. However, sputtering techniques pose a number of physical and engineering problems such as adhesion and reproducibility.

In general, the adhesion of inorganic layers to organic substrates is very poor. The lack of adhesion is due to the big difference in the surface energies and mechanical properties of the organic and inorganic phases. In the absence of chemical bonding, the adhesion is due to van der Waals forces only. Once deposited, the inorganic film is prone to rupture because of the difference in expansion coefficients between the coating and plastic substrates. Depositing an inorganic coating onto untreated PMMA or PC often results in a non-adhering layer that cracks due to thermal expansion, or in a fragile surface that is easily scratched. To qualitatively measure the adhesion between the AR coating and the substrate, we rubbing the sample with a hard cloth. Even after minutes of hard rubbing, the AR coating deposited on glass substrates didn’t presented signs of delamination. However, on plastic substrates, the adhesion strength was diminished.

A new method called liquid phase deposition (LPD) was recently developed
to deposit homogeneous SiO$_x$ layers onto plastic substrates [23, 24, 25, 26]. We used this method to improve the adhesion of silica–based nanoporous coatings to PMMA and PC substrates. A homogeneous SiO$_x$ film that is grown on the substrate, acts as an anchoring layer for the porous AR coating. Because the film has a similar refractive index as PMMA and PC (≈ 1.5), it has only a small influence on the optical properties of the coated surface.

The LPD method was developed by Nagayama et al. [23]. The advantage of the method is that it does not require expensive equipment and the deposition is performed at room temperature producing dense and homogeneous SiO$_x$ layers. The process involves the deposition and growth of a silica layer by immersing the substrate in an aqueous solution of hexafluorosilicic acid (H$_2$SiF$_6$) that is supersaturated with silica.

The silica saturation was obtained by dissolving a large quantity of fumed silica in the aqueous hexafluorosilicic acid solution (Fig. 4.7a). The plastic substrate was then immersed in the saturated solution and boric acid (H$_3$BO$_3$) was added to induce the supersaturation of the solution with silicon oxide (Fig. 4.7b). The chemical reactions responsible for the growth of the SiO$_x$ layer are

$$H_2SiF_6 + 2H_2O \rightleftharpoons 6HF + SiO_2$$  (4.10)
\[ \text{H}_3\text{BO}_3 + 4\text{HF} \rightleftharpoons 6\text{BF}_4^- + \text{H}_3\text{O}^+ + 2\text{H}_2\text{O} \quad (4.11) \]

Chou et al. [26] proposed an alternative explanation of the deposition process. Instead of Eqn. (4.10), they stated that the growth of SiO\textsubscript{x} film was dictated by the creation of intermediate SiF\textsubscript{m}(OH)\textsubscript{4−m} with \( m < 4 \). The corresponding reaction is:

\[ \text{H}_2\text{SiF}_6 + (4 - m) \cdot \text{H}_2\text{O} \rightleftharpoons \text{SiF}_m(\text{OH})_{4-m} + (6 - m) \cdot \text{HF} \quad (4.12) \]

When adding the boric acid, the HF is consumed and the intermediate SiF\textsubscript{m}(OH)\textsubscript{4−m} is created. The chemical reaction that describes this process is:

\[ \text{SiO}_2 : x\text{H}_2\text{O} + m \cdot \text{HF} \rightleftharpoons \text{SiF}_m(\text{OH})_{4-m} + (x + m - 2) \cdot \text{H}_2\text{O} \quad (4.13) \]

The intermediate SiF\textsubscript{m}(OH)\textsubscript{4−m} reacts either with the substrate to form silicon dioxide or with other SiF\textsubscript{m}(OH)\textsubscript{4−m} molecules to form a silica powder. The additional reactions of these molecules with the substrate are:

\[ \text{Si} - \text{F}_{\text{substrate}} + \text{Si} - \text{OH}_{\text{solution}} \rightleftharpoons \text{Si} - \text{O} - \text{Si}_{\text{substrate}} + \text{HF}_{\text{solution}} \]
\[ \text{Si} - \text{OH}_{\text{substrate}} + \text{Si} - \text{F}_{\text{solution}} \rightleftharpoons \text{Si} - \text{O} - \text{Si}_{\text{substrate}} + \text{HF}_{\text{solution}} \]

A schematic diagram illustrating the two routes to deposit SiO\textsubscript{x} layers on plastic substrates using the LDP method is depicted in Fig. (4.8).

The concentration of boric acid is much smaller than that of H\textsubscript{2}SiF\textsubscript{6}. As a consequence, only a small part of H\textsubscript{2}SiF\textsubscript{6} is transformed in the intermediate compound. Increasing the concentration of H\textsubscript{3}BO\textsubscript{3} leads to a higher concentration of SiF\textsubscript{m}(OH)\textsubscript{4−m} in the solution and a larger deposition rate. However, the disadvantage of increasing the deposition rate is a less dense and less homogeneous SiO\textsubscript{x} layer.

In our case, 800 ml pure hexafluorosilicic acid (34 %, 2.47 mol/l) was diluted with 200 ml water. The solution was then heated to 40° C and 30 g of silicon dioxide powder was added to saturate it. The mixture was stirred for 10 hours at 40° C and then filtered by centrifugation at 50.000 RPM.

The PMMA/PC substrates, were ultrasonically cleaned in a bath of ethanol and deionized water. Subsequently, the substrates were immersed in the coating solution at a temperature of 30° C. 0.2 mol/l solution of boric acid was
4.3 Experimental method

Figure 4.8: The schematic diagram illustrating the two routes to deposit SiO$_x$ layers on plastic substrates using the LDP method.

added in 5 consecutive batches of 1 ml each. After 5 h, the sample was taken out of the coating solution and rinsed with deionized water. The quality of the coating was tested by measuring the water contact angle on the substrate before and after deposition. The uncoated plastic substrate had a contact angle of $\approx 35^\circ$. The contact angle was close to zero for homogeneously coated plastic surfaces. The thickness of the deposited SiO$_x$ layer was $\approx 10$ nm, as measured by ellipsometry.

The SiO$_x$ film produced by LPD increased greatly the adhesion between the AR coating and the plastic substrate. By rubbing the sample with a hard cloth, the layer presented the same stability as the ones deposited on glass substrates. In addition, the film protected the substrates against the chemical
attack of the solvents in the AR coating solution.

In conclusion, the LPD technique proved to be an easy and straightforward method for coating plastic samples with an intermediary SiO$_x$ layer prior to deposition of AR coatings. The oxide homogeneity and thickness was found to depend on several factors such as deposition time, boric acid concentration, and temperature. By adjusting all these parameters, we were able to produce homogeneous 10 nm thick oxide films with a strong anchoring effect for the subsequently deposited antireflection coatings.

### 4.3.3 Improving the Cleanability of Porous AR Coatings

Adam and Wenzel [27] and Cassie and Baxter [28] showed that the apparent contact angle of a liquid droplet on the surface is correlated with the roughness of the surface. They demonstrated that water is repelled from rough, hydrophobic surfaces and water drops readily roll off. To be self-cleanable a surface has to fulfill two requirements:

- the water contact angle has to be higher than 170°
- the contact angle hysteresis must be small

The average roughness $R_a$ of a surface is defined as the arithmetic average of the absolute values of the surface height deviations measured from a mean plane. $R_a$ is given by

$$R_a = \frac{1}{N} \sum_{i=1}^{N} |z_i - \bar{Z}|$$  \hspace{1cm} (4.14)

with

$$\bar{Z} = \frac{1}{N} \sum_{i=1}^{N} z_i$$  \hspace{1cm} (4.15)

where $i$ is the number of measurements and $N$ is the number of data points.

The porous silica AR coatings produced by both methods described in Section 4.3.1 had a roughness of $\approx 1.6$ nm, as measured by AFM. Due to their high surface energy, the effect of the roughness is to decrease the water contact angle. To increase the water contact angle,

3-Heptafluoroisopropoxypropyltrimethoxysilane (HFIPP-tMOS)
was added to the TMOS precursor in a weight ratio of 1:20, before the acid addition.

Due to the methoxy groups, the new component hydrolyzes and condenses in the same manner as TMOS. After completing the reactions, the sol solution contained particles that were partly fluorinated. The AR coating morphology was dictated by the free energy of the system during the spin–coating process. The fluorinated part with low surface energy preferred the air–film interface while the unfluorinated sols preferred the substrate. This way, by exposing the fluorinated parts to the air surface, the measured contact angle increased from 7° to 130° (Fig. 4.9). The value of the contact angle was still too low for the surface to have self-cleaning properties. The combination of a low energy surface and high roughness led, however, to improved cleaning properties of the AR film. A finger print could easily be washed off by a mixture of water and ethanol (3:1 by weight).

4.4 Conclusions

The work in this chapter describes a new method of producing low cost, broad–band antireflection coatings. Our approach made use of a simple prin-
ciple – the demixing process between an organic phase (PAA/PMMA) and an inorganic phase (silicon dioxide sols). The resulting AR coatings were easily fine-tuned to produce a wide range of refractive indices. The sizes and density of the pores were varied by varying the molecular weight and the amount of the polymeric phase. The thickness of the layer was adjusted by varying the spin-coating speed. In this manner, the light transmission at selected wavelengths was enhanced. The optical properties of the mineral nanoporous AR coating proved to be superior to the standard MgF$_2$ coatings. The light transmitted through a coated surface varied only little with the incident angle. The coatings had good mechanical stability on glass, strong adhesion to plastic substrates and improved cleanability.
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