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Antireflective coatings prepared by sol–gel processing: Principles and applications

Walther Glaubitt, Peer Löbmann *

Fraunhofer-Institut für Silicatforschung, Neunerplatz 2, 97082 Würzburg, Germany

Abstract

Sol–gel processing is a powerful tool to prepare antireflective (AR) coatings on optical surfaces. In this paper the different strategies to obtain antireflective properties are reviewed: porous λ/4 layers, multilayer interference-type films and index-gradient materials such as "moth eye" structures. The processing of the respective films is described and evaluated; references to respective commercial products on glass substrates are given.

AR coatings may have a particularly high importance for transparent ceramics as their index of refraction is significantly higher than that of common glass types. Reflective losses therefore are higher which is especially unpleasant for materials with a yet improvable intrinsic transparency.

Recent studies indicate that specific porous λ/4 layers may exhibit pronounced anti-soiling features. Laboratory experiments as well as outdoor exposure tests were used to demonstrate the dust-repellant properties.

Keywords: Thin films; Antireflective coatings; Sol–gel processing

1. Introduction

When light passes the border between different optical media, it is at least partially reflected. When the incident medium is air with a refractive index $n_0 = 1$, the reflectivity R is calculated as

$$R = \left[\frac{1 - n_{\text{substrate}}}{1 + n_{\text{substrate}}}\right]^2 \quad (1)$$

for any substrate according to the Fresnel equations.

In order to reduce reflection a film with intermediate index of refraction can be applied according to Fig. 1. If the optical film thickness ($d \times n_{\text{film}}$) is 1/4 of the wavelength, the phase difference becomes π and the two reflected waves cancel out. For complete annihilation, the amplitude of the interfering radiation also has to be identical. This requirement is fulfilled when the refractive index of the film is equal to the square root of the refractive index of the substrate.

The complete transmission of light with a wavelength of 550 nm thus requires film material with a refractive index of 1.22 and a layer thickness of 112.7 nm according to Fig. 1. For light with any other wavelength, a higher reflection will be observed; the bandwidth of the AR coating is limited.

General guidelines for antireflective films can be derived from these argumentations. Wave angle dependencies, optical dispersion in the different media, and adsorption phenomena, however, have to be considered for an exhaustive description of reflection phenomena and sophisticated product design.

Dense materials with an index of refraction as low as 1.22 are not available, therefore, porous films have to be applied as λ/4-layers.

Alternating stacks of low- and high refractive materials such as SiO_2 and TiO_2 may be used for the production of interference-type multilayer assemblies. With such design, zero-reflection is approached for more than one wavelength which increases the spectral bandwidth.

As an alternative strategy, films with a continuous gradient of refractivity may provide antireflective properties: A gradual decrease of n_{film} from $n_{\text{substrate}}$ to unity optically matches the substrate to the ambient atmosphere resulting in optical neutrality. For example, pyramidal surface structures represent a gradual lateral increase in space-filling from the upper surface of the film to the bottom of the structure. Antireflective properties, however, are only expected for sizes below the incident wavelength, otherwise scattering will occur.

* Corresponding author.
E-mail address: peer.loebmann@isc.fraunhofer.de (P. Löbmann).

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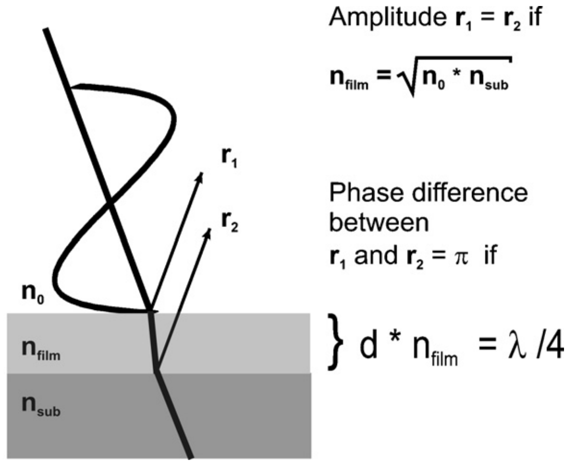

Fig. 1. Transmission of light through a thin film and conditions for destructive interference.

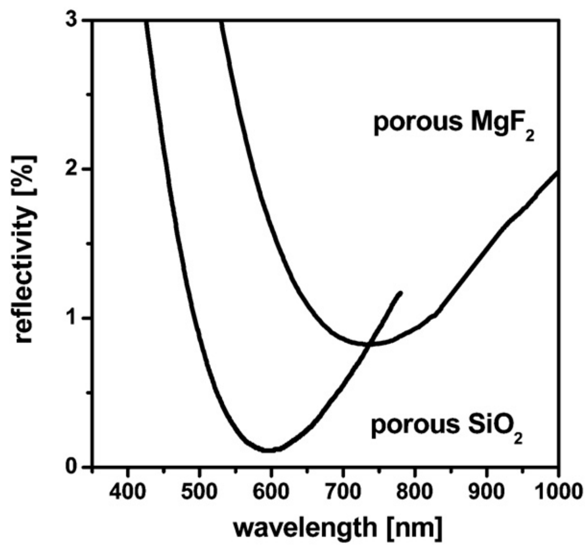

Fig. 2. Reflectivity of porous SiO_2 and MgF_2 λ/4 AR coatings.

However, there will be scattering if such structures are too large. Biological examples of such antireflective surfaces are known from the compound eyes of insects (“moth eye” structures).[1]

All strategies for anti-reflection coatings described here can be realized by sol–gel processing. In the following paragraphs, the respective techniques will be described and references to commercial products will be given.

2. Porous AR films

Introducing porosity into a film will decrease its index of refraction n_{film}. For materials such as SiO_2, Al_2O_3, and TiO_2, commonly used in sol–gel processing, porous λ/4 films for a variety of substrates are conceivable when the respective refractive indices are taken into consideration. For common glasses ($n \sim 1.46$–1.65) SiO_2 turns out to be most suitable because the required porosities around 50% may provide a satisfactory mechanical stability.

With $n = 1.38$ magnesium fluoride has a significantly lower index of refraction than SiO_2 ($n = 1.5$), MgF_2 films with lower porosity and therefore higher mechanical stability, would allow higher transmissions. Recently, the wet chemical preparation of MgF_2 precursor solutions has been reported.[2] In Fig. 2 the optical spectra of some porous SiO_2 and MgF_2 are given.

The idea of porous SiO_2 AR coatings by wet-chemical deposition dates back to 1949.[3] However, the disadvantage caused by their limited mechanical stability has prevented widespread applications up to now. Even though such coatings may well resist “normal” handling and weathering, mechanical cleaning that often goes along with the unintentional reaming of abrasive particles (soil, dust) will damage the films. Therefore, applications such as displays, architectural or automotive glazing are difficult to address with porous systems.

Solar panels, though, seldomly undergo mechanical cleaning. Porous λ/4 films therefore are suitable to increase the efficiency of solar modules. In 2008 Centrosolar Glass (Fürth, Germany) produced 2,000,000 m^2 of porous AR coatings by dip-coating. In Fig. 3 the photograph of a solar panel equipped with an AR film is displayed. Such films exhibit excellent transmittances with a refractive index of 1.22 even after 8 years outdoor exposure.

It is worth mentioning that it took over half a century from the first patent describing the concept of porous AR coatings[3] to the development of coating procedures that meet the requirements of a practical application[4] and successful commercialization.[5]

3. Interference-type multilayers for AR applications

Alternating stacks of low- and high refractive materials are required for the production of interference-type multilayer AR films.

SiO_2 is commonly used as low-index material. In contrast to the preparation of porous λ/4 layers, dense microstructures are desirable for a good mechanical stability of the multilayer stacks. Therefore, acid-catalyzed hydrolysis and condensation

Fig. 3. Solar panel equipped with porous λ/4 glazing Image: © Centrosolar Glas GmbH & Co. KG, Germany.

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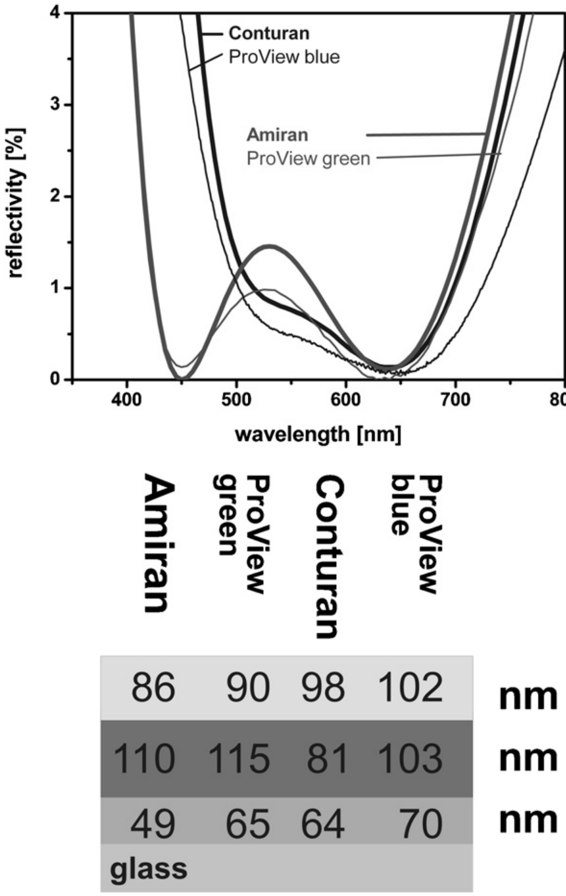

Fig. 4. Reflectivity of commercially available triple layer AR coatings (*top*) and associated stack architectures (*bottom*). *Data*: Schott AG (Amiran® and Conturan®) and Prinz Optics (ProView green and blue), Germany.

reactions are employed to ensure optimum densification of the films that easily exhibit optical properties of silica glass.

In contrast to SiO_2, that remains amorphous throughout processing, TiO_2 has to be crystallized in order to attain the desired high index of refraction.

For optimum performance, 3-layer AR coatings require the deposition of a film with medium refractive index on the substrate below the successive TiO_2 and SiO_2 layers. Such materials may be obtained by the synthesis of coating solutions aiming at a mixed composition of SiO_2 and TiO_2 or ZrO_2 because the proportions add up linearly to the resulting index of refraction.

In Fig. 4 the optical spectra of some commercially available 3-layer antireflective coatings is summarized along with their layouts as provided by the suppliers. Conturan® and AR4 are designed for cover glasses of instrumentations whereas Amiran® and AR2 are mostly applied in architectural glazing. Due to their spectral characteristics, white light reflected from these surfaces appears tinted slightly bluish and greenish respectively.

4. Surface patterning – "moth eye" structures

In 1967 it was observed that the reflection from the compound eyes of some moths is significantly reduced by microscopic surface structures which provide them with reduced visibility to predators at nighttime.[6]

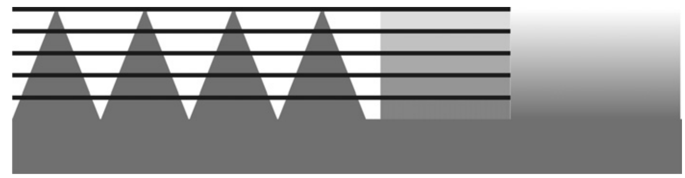

Fig. 5. Schematic representation of refractive index from pyramidal surface pattern.

Fig. 5 provides a schematic representation of the related working principle. Any surface structure can be divided into horizontal segments that optically are an average mixture of solid and the environment. A mean index of refraction may be assigned to each slice. In the case of a pyramidal shape the upper slices mainly consist of air with some minor contribution of the solid, whereas the lower parts come close to the refractive index of the substrate. If the distance between the neighboring structures is below the wavelength of the incident light, no scattering will occur.

It is possible to prepare artificial moth eye structures by the embossing of sol–gel films prior to thermal curing. The tools required are obtained by casting of polymer materials by master

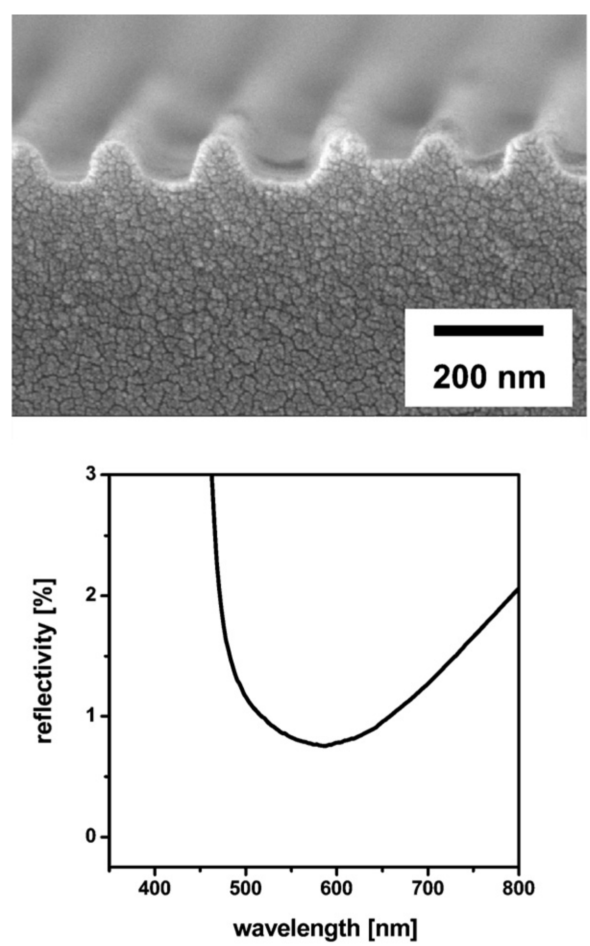

Fig. 6. SEM image of a linear grating (*top*) and reflectivity of a cross-grating (*bottom*) both prepared by sol–gel processing.

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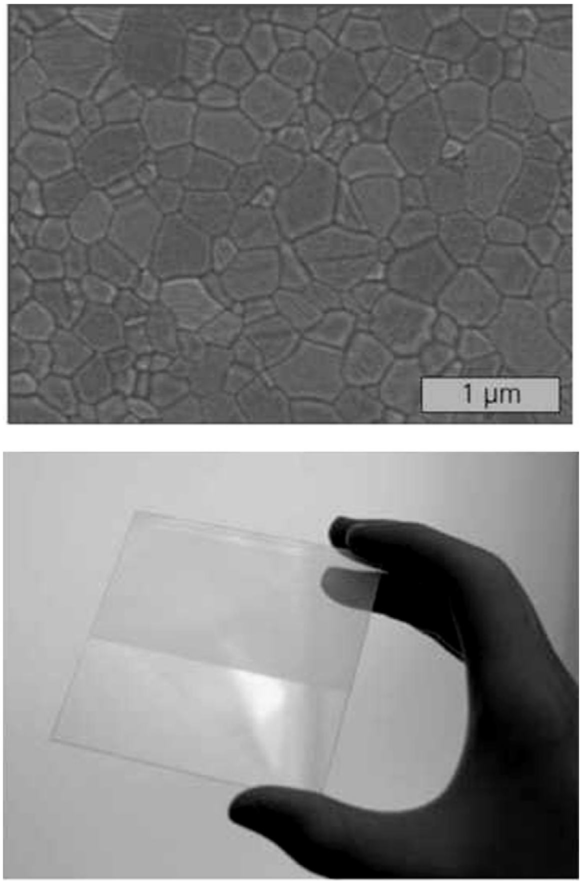

Fig. 7. SEM surface micrograph of transparent corundum ceramic (*top*) and photographic image of sample partially coated with porous AR λ/4 film (*bottom*). Images courtesy of FhG-IKTS (Dresden).

structures derived from photolithographic processes. In Fig. 6 the SEM image of such a linear grating is given along with the reflectivity of a similar cross-grating.

Even though, reflectivities below 1% are achieved for wavelengths in the visible region, the optical performance remains below porous antireflective coatings. This is partially due to still insufficient depths of the structure. This shortcoming may be compensated by an improved mechanical stability. Yet, limited bandwidths are associated with suboptimal patterns shape.

It has to be noted, though, that the large-area processing of embossed sol–gel coatings still remains a technological challenge.

5. AR coatings on transparent ceramics

Since the refractive index of most ceramic material is significantly higher than that of technical glasses, a higher reflectance occurs at the respective solid–gas interface. Accordingly porous SiO_2 λ/4 layers with a lower porosity than required for glass are able to provide antireflective properties.

In Fig. 7 the surface image of a transparent corundum ceramic is given along with a photograph of a sample half-coated with a porous AR film.

For best λ/4 antireflective coating corundum ($n = 1.77$) requires a film with $n = 1.33$. Therefore SiO_2 films with 30% porosity were applied by sol–gel processing. The image in Fig. 7 (bottom) demonstrates the reduced reflection of the upper part of the sample which is covered by the film.

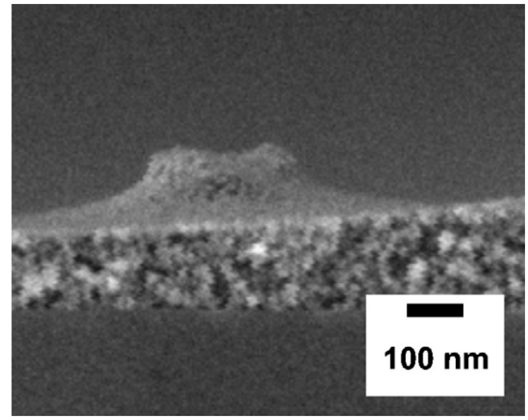

Fig. 8. SEM image of a porous AR film modified by the incorporation of large SiO_2 particles.

6. Dust-repelling AR coatings

So-called “self cleaning surfaces” have gained a lot of public and scientific attention since it was recognized that certain plant surfaces remain astonishingly unstained in their natural environment.[7] The so-called “Lotus Effect” is based on the fact that water is repelled from the micropatterned hydrophobic leaf surfaces. In that context, solid contaminations have a reduced attachment to these surface topographies and are easily removed by water droplets. However, since large patterned surfaces are difficult to prepare on a commercial scale and microstructures in the dimensions observed on plant surfaces scatter light, traditional “Lotus surfaces” cannot be used for applications were transparency is required.

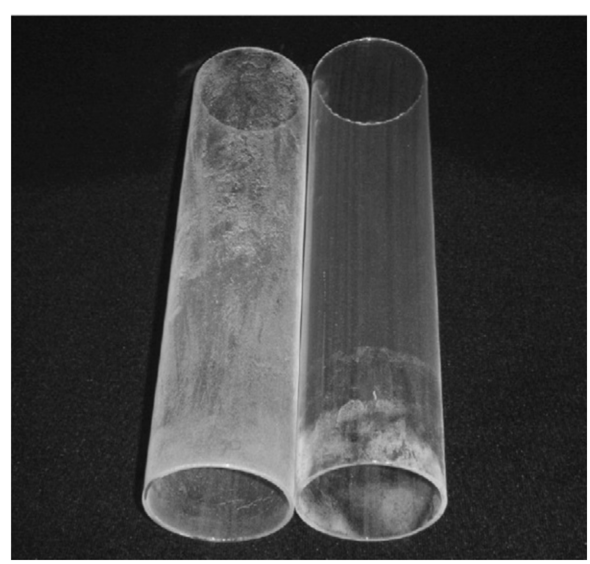

Fig. 9. Photographic image of an uncoated glass tube (*left*) and a glass tube coated with an anti-soiling film (*right*). The stained areas of latter sample in the lower part correspond to the segment that remained uncoated during the dip-coating experiment.

Silica particles with average diameters of 60 nm were incorporated into coating solutions for the preparation of porous AR films.[8] The SEM image of a resulting film is given in Fig. 8. It can be seen that the surface of AR film is corrugated by these particles, but they are covered by the fine-grained matrix material. Since the particles are much smaller than the visual wavelength, these films retain their antireflective properties.

It was noted on an empirical basis, that the combination of some SiO_2 particle sizes with certain matrix systems result in coatings that show distinct anti-soiling properties both in laboratory experiments and during long-term outdoor exposure. Fig. 9 shows such a film compared to an uncoated glass tube.

Even though up to now no comprehensive explanation of the observations can be presented, the anti-soiling effect is believed to originate from the cooperative effect of large and short range surface roughness generated by the SiO_2 nanoparticles and the matrix system.[8]

7. Conclusions

The full width of strategies for the preparation of antireflective surfaces reaching from porous λ/4 films, dense multilayer interference filters to nanostructured surface patterns can be accomplished by sol–gel techniques.

It is remarkable, though, that in the case of for example porous AR coatings, a time span of half a century lies between first patents and final commercialization. “Boring” and academically ungrateful work regarding solution stability, upscaling of synthesis and coating technology, adhesion, mechanical stability, and weathering resistance, contribute to such a tardy economic impact.

Nevertheless, many novel approaches such as the preparation of porous MgF_2 films and dust-repellent AR coatings will provide vast chances of commercial success in the near future.

References

1. Wilson SJ, Hutley MC. The optical properties of ‘moth eye’ antireflection surfaces. *Opt Acta (Lond)* 1982;**29**:993–1009.
2. Krüger H, Kemnitz E, Hertwig A, Beck U. Transparent MgF_2-films by sol–gel coating: synthesis and optical properties. *Thin Solid Films* 2008;**516**:4175–7.
3. Moulton H. *US Patent* 2,474,061 (1949).
4. Glaubitt W, Kursawe M, Gombert A, Hofmann T. Novel hybrid sol for producing abrasion-resistant SiO_2 antireflection coatings on glass. PCT/EP 2002/010492; 2002.
5. Gombert A, Glaubitt W. Antireflective transparent coatings for solar devices. *Solar Energy* 2000;**68**:357–60.
6. Bernhard C. Structural and functional adaption in a visual system. *Endeavour* 1967;**26**:79–84.
7. Barthlott W, Neinhuis C. Purity of the sacred Lotus, or escape from contamination in biological surfaces. *Planta* 1997;**202**:1–8.
8. Glaubitt W, Löbmann P. Anti-soiling effect of porous SiO_2 coatings prepared by sol–gel processing. *J Sol-Gel Sci Technol* 2011;**59**:239–44.

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