Sol-gel deposition of nanostructured low refractive index materials on solar collector glazing

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Abstract

Nanoporous SiO_2 and nanocomposite MgF_2:SiO_2 coatings have been deposited by sol-gel dip-coating in a particle-free atmosphere. The refractive index of the prepared nanostructured thin films is determined from spectrophotometric data. In both cases, significantly lower values than for compact SiO_2 have been achieved. Highly transparent samples have been produced in a single dip-coating step followed by simple thermal annealing in air. Broad spectral transmittance maxima are observed exceeding values of 98.5% (nanoporous SiO_2) and 99.5% (quaternary Mg:F:Si:O films). MgF_2:SiO_2 nanocomposite thin films can be expected to exhibit a higher aging stability than porous SiO_2 films with respect to pore-filling by hydrocarbons and are therefore a promising alternative as well for single-layered anti-reflection coatings as for multilayered coulored coatings on solar collector glazing.

Keywords: anti-reflection, solar collector glazing, nanoporous materials, nanocomposite thin films, sol-gel dip-coating

1. Introduction

Thin film materials exhibiting a low refractive index are of special interest for coatings on solar collector glazing [1-4]. Anti-reflection coatings on solar thermal collector glazing should be efficient in the full spectral range of terrestrial solar radiation. Applying materials with a lower refractive index than silicon dioxide (refractive index approx. 1.46) allows for a larger spectral region of anti-reflection as compared to coatings based on materials with the refractive index equal or higher than that of silicon dioxide. Recent simulations [5,6] showed that low index materials will also be useful for the application in coatings on glazing for coloured facade collectors. Multilayered oxide coatings for coloured collectors have been obtained by magnetron sputtering [7] and by sol-gel dip-coating [8]. If lower refractive indices than that of SiO_2 were available, a higher solar transmittance could be achieved for the same value of visible reflectance due to partial anti-reflection in spectral regions neighbouring the VIS reflectance peak.

One way to achieve a lower index than that of SiO_2 is to introduce voids into the material [9]. If scattering is undesired, the pores should be clearly smaller than the wavelength of the considered light. Nanostructured silicon oxide films can be produced by sol-gel manufacturing (see e.g. refs. [10,11]), or by holographic patterning [12], and are entering the market of solar thermal collectors and PV glazing. Therefore durability testing of such coatings is highly important [13]. Critical issues here are the mechanical stability of such porous films [14] and the risk of pore-filling by hydrocarbons.

Coatings with a refractive index lower than that of compact SiO_2 are conventionally produced from magnesium difluoride MgF_2 (refractive index approx. 1.38) by thermal evaporation [15]. However, the mechanical properties of MgF_2 are less advantageous than those of compact silicon dioxide, which surpasses MgF_2 in hardness and abrasion resistance [16]. Having in mind the thermal annealing step following the dip-coating, the sol-gel fabrication of non-oxides is less obvious, but in the case of MgF_2 not impossible [17,18]. The different methods for MgF_2 deposition are compared in [19].

Relatively little information on the fabrication of quaternary Mg:F:Si:O films can be found in the literature. Rywak et al. [20] report on the sol-gel deposition of MgF_2-SiO_2 composite films by sol-gel dip-coating. Evidence for the presence of MgF_2 nanocrystals immersed in a matrix of amorphous SiO_2 was strongly suggested by the analysis of XRD data, but no refractive index data are presented in ref. [20].

The aim of this work is to compare the possibilities of reducing the refractive index of silicon dioxide by introduction of voids or clusters of magnesium fluoride. We report on the sol-gel fabrication of nanoporous SiO_2 and nanocomposite MgF_2:SiO_2 coatings, and on the optical characterisation of the obtained films by spectrophotometry.

2. Experimental

2.1 Sample preparation

Solutions for sol-gel dip-coating have been prepared in a laminar flux chapel on the basis of the precursors tetraethyl orthosilicate (TEOS, $C_8H_{20}O_4Si$), magnesium acetate tetra hydrate ($C_4H_6O_4Mg \cdot 4\ H_2O$) and trifluoroacetic acid (TFA, $C_2HF_3O_2$), using ethanol and isopropanol as solvants.

For the preparation of solutions suitable for the deposition of porous SiO_2, TEOS has been hydrolyzed in presence of nitric acid HNO_3 and water H_2O. As structuring agent, polyethylene glycole (PEG, average molar weights 200, 400, 600, and 1000) is used. During hydrolysis, the solution is stirred and heated to 50°C for a period of several hours. For the synthesis of magnesium fluoride based films, magnesium acetate tetra hydrate, trifluoroacetic acid, isopropanol and H_2O are mixed and the solution is stirred during several hours. After hydrolysis, both components can be mixed in the desired molar ratio for synthesis of quaternary Mg:F:Si:O films. Triton-x-100 is always added in order to improve the wettability in the following process. After aging for several days, the solutions are used in the dip-coating process.

In order to achieve a vibration-free and regular movement for the dipping and withdrawal of the substrates, a suitable apparatus has been developed. A servo drive (MKD 25B REXROTH) is controlled by a feedback loop (control unit Ecodrive 03 REXROTH INDRAMAT). The speed of the rotation is adapted by a Neugart transmission and transformed into a translational movement by a helix equipped with a special ball bearing (compact module CKK 12-90, REXROTH). A microcomputer is used to command the control unit of the servo drive. For this purpose, a program has been written in Labview, which allows a user-friendly operation in the laboratory. The dip-coater has been designed for a maximum substrate size of 20 cm x 30 cm, but in early stages of process development also smaller substrates such as microscope slides (ca. 76 x 26 x 1 mm^3) and float glass samples of intermediate dimensions (70 x 60 x 4 mm^3) are used. For dust-protection the dip-coater is placed in a laminar flux chapel (SKANAIR VFC 120). The air quality is monitored by real-time particle counting (KLOTZ PSSair with isocinetic nozzle). In the laminar flux chapel typically less than 1 particle larger than 0.3 micron is counted per cubic feet (for comparison: ambient laboratory air: ~ 104 particles per cubic ft). After dip-coating, the resulting thin xerogel films are tempered typically at 200°C - 400°C in air. During thermal annealing, samples are enclosed in special containers to avoid dust contamination during sample transfer and tempering. Before dip-coating, substrates are cleaned thoroughly in an ultrasonic bath (BRANSON 8510).

2.2 Refractive index determination

Spectral transmittance and reflectance measurements of the produced samples have been performed in the VIS range (380 nm to 820 nm) by a grating spectrophotometer (ORIEL MS 125TM 1/8m Spectrograph, with a InstaspecTM II Photodiode Array Detector and sighting optics). A silicon monocrystal serves as reference sample for reflectance measurements with well-known optical properties [21]. The precision of the measurements of the normal spectral transmittance has been estimated from reproducibility tests to the order of 0.3 to 0.5 percentage points.

The refractive index of the thin films deposited symmetrically on both sides of the glass substrate by sol-gel dip-coating has to be inferred from optical measurements. Taking into account infinite multiple reflections between the two symmetric sides of the substrate, the relation of the transmittance t of a film on one surface of the glass (air//film//glass) can be related to the transmittance T of the total system (air//film//glass//film//air) by the simple expression:

$$t = \frac{2T}{(1+T)} \qquad \text{eqn.1}$$

For transparent thin films and substrates, the intensity t_{max} of the maximum in transmittance t can be calculated from the refractive indices n, n_g, n_m of thin film, substrate and surrounding medium (case $n < n_g$, compare to refs. [22,23]):

$$t_{\max} = \frac{4 n_m n^2 n_g}{(n_m n_g + n^2)^2} \qquad \text{eqn.2}$$

By inverting this relation, the refractive index n can be found precisely and with high certainty for the wavelengths where transmission maxima are occurring.

3. Results and Discussion

3.1 Porous SiO_2 films

Pourous SiO_2 films could be produced from solutions based on PEG 200, 400, 600 and 1000. Very encouraging results have been found for PEG 600. The pore formation during thermal annealing of PEG 600 containing xerogel films is illustrated in Fig.1. Shown are normal transmittance spectra after tempering the samples in air at 200°C, 350°C, 450°C and 550°C, respectively. Even though annealing at 200°C leads to a general decrease in normal transmittance, the transmittance rises again for higher annealing temperatures. For annealing at 550°C a large transmittance maximum exceeding 98.5% is reached at a wavelength of approximately 550 nm, which perfectly corresponds to the maximum in terrestrial solar radiation. The initial decrease in solar transmittance can be explained by the assumption that the film densifies before the PEG molecules are oxidized, leaving nanometric pores behind. No light diffusion was observed, confirming that pore sizes must be well below the wavelength of visible light.

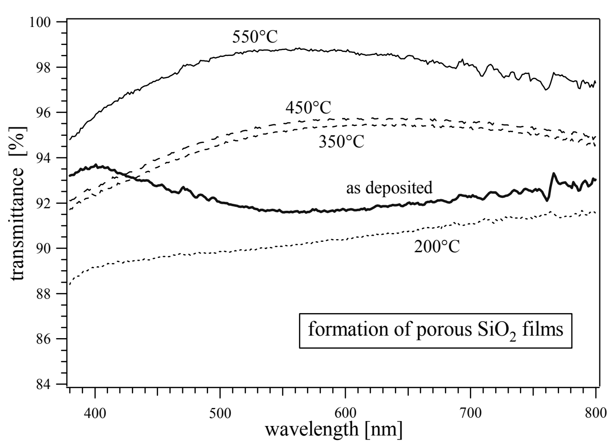

Fig.1: Evolution of normal transmittance spectra during pore formation in silicon oxide based films (spectra as deposited and after one annealing step at 200°C, 350°C, 450°C and 550°C, respectively). After tempering at 550°C the spectral transmittance at wavelengths around 550 nm exceeds 98.5%.

3.2 MgF_2 films

The wettability of the used solutions used for MgF_2 synthesis appeared to be somewhat critical and not always satisfying. For thermal annealing in nitrogen, a special reactor was used, but the optical results for the refractive index strongly suggest that for the formation of MgF_2 films normal tempering in air is sufficient. Fig. 2 illustrates the dispersion relation n(λ) of likewise prepared films. The results for thermal annealing 300°C are rather close to refractive index values reported in the literature [15]. A dependence of the refractive index on the annealing temperature is observed, raising the question whether at 400°C a small volume fraction of pores is formed. Due to the observed wettability problems and haze formation during annealing, the quality of the deposited thin films was rather moderate compared to the porous silicon oxide films.

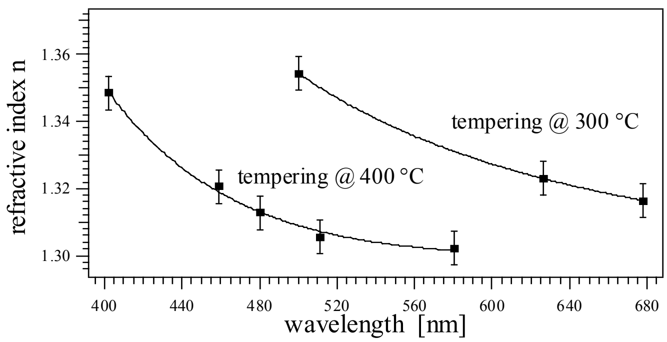

Fig.2: Dispersion relation n(λ) of sol-gel deposited MgF_2 films formed by thermal annealing in ambient air. The values of the refractive index are close to the range expected for MgF_2 thin films [15]. A dependence of n(λ) on the annealing temperature is observed.

3.3 Quaternary Mg:F:Si:O films

Precursor solutions have been developed which are compatible with each other when mixing them after separate hydrolysis. Annealing can be performed simply in ambient air. Due to a better wettability, the dip-coating process turned out to be much less difficult than for the pure MgF_2 precursor solution. In addition, the tendency to haze formation is much lower, yielding a considerably higher film quality. Energy dispersive X-ray analysis (EDX) confirmed the presence of Mg, F, Si and O in the deposited films. Samples could be prepared to be highly transparent, as illustrated by Fig.3. The chemical composition of the films corresponds to a nominal molar ratio MgF_2 : SiO_2 of 1:1. The displayed curves exhibit broad transmittance maxima exceeding 99.5%. By varying the withdrawal speed in the dip-coating process, the film thickness has been varied from 99 nm to 124 nm. For the film thickness of 113 nm, a transmission maximum close to 99.9% is observed in the spectral region around the wavelength of 600 nm.

Using eqns. 1 and 2, the refractive index of the quaternary thin films has been determined from normal transmittance spectra for a large set of samples, varying film thickness and chemical composition. In Fig. 4 the refractive index at the wavelength of 685 nm is plotted as a function of the nominal molar ratio MgF_2 : SiO_2 . Refractive index values considerably lower than that of pure SiO_2 have been achieved, the lowest for equal molar concentrations of Si and Mg (corresponding to 50% molar fraction SiO_2). This result appears as surprising, since Bruggeman and Ping Sheng effective medium theories [24,25] do not predict such a highly pronounced refractive index minimum in the observed range for compact MgF_2/SiO_2 two-phase materials. Possible explanations might be the occurrence of nanometric pores or the formation of ternary or quaternary phases. Preliminary results in transmission electron have confirmed the assumption of a nanostructured material containing more than one phase. Further investigations will be necessary to study the nanostructure of this interesting new material in detail. If there are less open pores in such quaternary films than in porous SiO_2 with comparable refractive index, a higher resistance with respect to pore filling by hydrocarbons can be expected, as well as easier applicability in multilayer stacks.

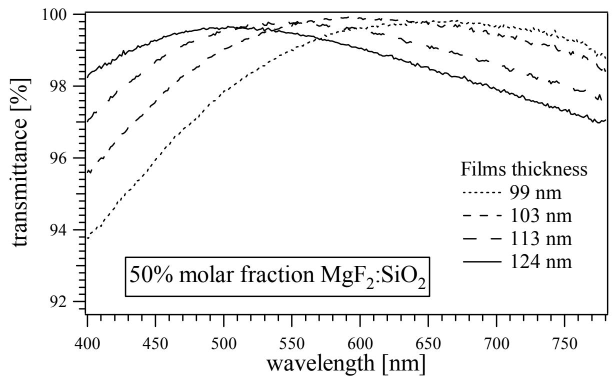

Fig.3: Normal transmittance of quaternary thin films based on the elements Mg, F, Si, and O. The molar fractions correspond to a nominal molar ratio MgF_2 : SiO_2 of 1:1. Broad transmittance maxima exceeding 99.5% are observed.

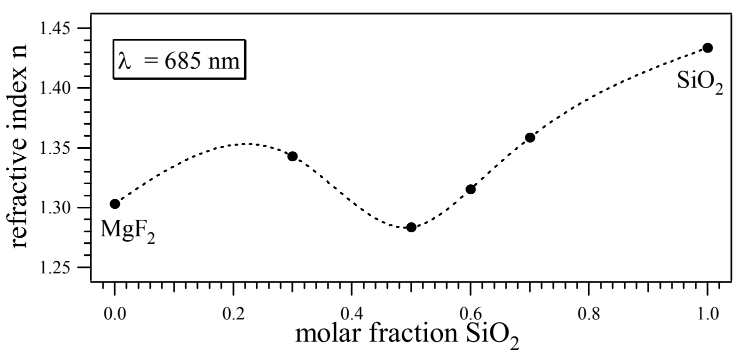

Fig. 4: Refractive index at 685 nm as a function of the chemical composition of quaternary Mg:F:Si:O films. Values considerably lower than that of pure SiO_2 have been achieved, the lowest for equal molar concentrations of Si and Mg (corresponding to 50% molar fractions MgF_2 and SiO_2). The dotted line serves as guide to the eye.

4. Conclusion

Nanoporous SiO_2, MgF_2 and quaternary Mg:F:Si:O films were prepared by sol-gel dip-coating and subsequent thermal annealing. Not only the oxide but also the fluoride based films can be formed by simple annealing in ambient air which does not require complex installations for providing any inert gas atmosphere. The use of hydrofluoric acid HF can be avoided for the production of fluorine based coatings. The refractive index of SiO_2 can be lowered considerably by the introduction of voids, resulting in highly transparent samples. The durability of such films remains an issue (hardness, danger of pores filling up with hydrocarbons), as well as their applicability in multilayer stacks. Pure MgF_2 coatings represent a rather compact but soft material with a refractive index lower than that of SiO_2. The wettability of the used solutions appears somewhat critical and not always satisfying. In contrast to that, the wettability of the precursor solutions for quaternary Mg:F:Si:O films is much less critical, which holds also for haze formation during thermal annealing. Such films represent a tuneable low-index system, with a refractive index even considerably lower than expected. The coating hardness can be expected to be higher than that of pure MgF_2 and porous SiO_2 films. In addition, the risk of degradation by pore-filling by hydrocarbons might be considerably lower than for porous SiO_2. The system might also be more suitable for application in multilayers. Exciting new possibilities for the development of single- and multilayered coatings for anti-reflection and/or colouration of solar collector glazing have thus been opened by this promising novel material. However, the optical results imply that further studies of the nanostructure will be necessary for understanding the material properties.

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