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ORIGINAL PAPER: FUNCTIONAL COATINGS, THIN FILMS AND MEMBRANES (INCLUDING DEPOSITION TECHNIQUES)

Solubility of porous MgF_2 films in water: influence of glass substrates

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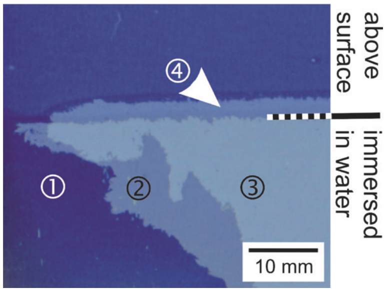
Abstract MgF_2 antireflective coatings exposed to cold water show an increase of porosity and film delamination after prolonged soaking times. The related structural changes within the material were characterized by scanning electron microscopy and ellipsometric porosimetry. The glass substrate type used, namely its sodium content, has a pronounced effect on the film microstructure and its long-term solubility. The stability of MgF_2 films could significantly be improved by Na-doping of the coating solutions.

Graphical Abstract Porous MgF_2 prepared by sol-gel processing dissolve and delaminate after prolonged exposure to water at room temperature. This behavior is influenced by different glass substrates; film stability can be significantly improved by doping of sodium to the coating solutions.



Keywords MgF2 · Antireflective coatings · Film dissolution · Doping

1 Introduction

Antireflective (AR) coatings are of high importance for photovoltaic modules, ophthalmic lenses, architectural glazing, display applications and other optical devices. Besides vapor-based methods, the sol-gel processing from liquid precursors has proven to be a viable tool for the realization of different concepts such as interference AR filters, index gradient films and λ/4 single layers [1]. As for the latter approach, thin porous materials are required [2, 3]; their mechanical stability is an important issue. Therefore even though porous SiO_2 has been realized as AR films on solar panels [1, 3], applications that are subjected to harsher mechanical cleaning conditions such as windows or displays are up to now not yet equipped with λ/4 layers.

Use of SiO_2 with a backbone refractive index of ~1.5 porosities of around 50% is required for optimum optical performance on common glass substrates. This value can be reduced to ~30% by applying MgF_2 with a solid refractive index of 1.38. This decrease in porosity offers good perspectives for a significant improvement of mechanical stability. In this course, porous MgF_2 coatings have been developed [4–7], some of them showed a remarkable resistance to crockmeter-testing even using steel wool as abrasive [8]. Additionally, a steady-state temperature humidity life testing (“85/85”) has been passed successfully [9].

In this paper, we describe the effect of soaking porous MgF_2 coatings in cold water. It is shown that sodium

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diffusion from the substrate into film during thermal curing has a pronounced impact on its nanostructure and resulting stability.

2 Experimental procedure

2.1 Precursor synthesis

All chemicals for the preparation of magnesium fluoride precursor solutions were used as received without drying or further processing. For better handling and dosing, the HF solution used for these experiments was prepared by condensation of HF (Solvay Fluor GmbH, Hanover, Germany) in ethanol with a 19.2 M concentration. Details regarding the synthesis are disclosed elsewhere [10]; all related procedures were carried out at the Humboldt University Berlin (Berlin, Germany). The MgF_2 coating solutions were doped by addition of 1–2 mol% NaOAc (Aldrich) with respect to the Mg-content.

2.2 Film preparation

The MgF_2 thin films were prepared by dip coating on borosilicate glass (Schott Borofloat$^{®}$), soda-lime glass (Eurofloat$^{®}$, Euroglas) and display glass (Eagle XG, Corning) at the size of $3.3 \times 150 \times 100\ mm^3$.

Before the coating experiment, the different substrates were cleaned in a laboratory dishwasher by an alkaline cleaning procedure with a final neutralization step. After coating, the samples were pre-dried for 10 min at 80 °C in a vented furnace (Model D-6450, Heraeus Instruments, Hanau, Germany). Final curing was performed by placing the samples in an oven (Model Thermicon P, Heraeus Instruments, Hanau, Germany) at ambient conditions. Then the temperature was raised to 500 °C within 2 h. After a dwell time of 10 min, the samples were allowed to cool down to room temperature overnight.

2.3 Material characterization

In-plane surfaces of the films were examined by scanning electron microscopy (SEM), using a Zeiss Ultra 25 (Carl Zeiss SMT, Oberkochen, Germany). Pt was applied prior to the investigation by sputtering.

Open porosity was determined with atmospheric ellipsometric porosimetry (EP), which uses the change of the refractive index ($n_{(633\ nm)}$) during water-vapor adsorption and desorption [11, 12]. Before measurement, the samples were rinsed with de-ionized water, immersed for 5 min in Ethanol and dried for 5 min at 180 °C in a vented furnace. To calculate open porosity, the ellipsometric results of completely empty pores and fully water-filled pores can be evaluated with Lorentz-Lorenz equation, without requirement of any information of the backbone material.

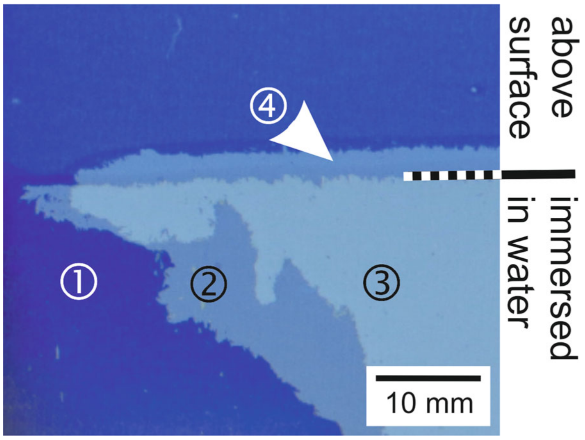

Fig. 1 Photo of borosilicate glass substrate coated on both sides with MgF_2 after partial immersion in water: ① intact films, ② delaminated from one side and ③ both sides delaminated. In position ④ the film is damaged due to water undulation near the surface of the water bath (Color figure online)

XPS measurements were performed on a X-Ray photoelectron spectrometer (Model X-Probe, Surface Science Instruments, California) using monochromated Al K_α radiation. For depth profiling, a sputtering source (Leybold-Heraeus Model IQE) at operation voltage 5 kV was used.

3 Results and discussion

Sol-gel-derived MgF_2 films previously have shown good stability in steady-state temperature humidity life testing [9]. Outdoor exposures experiments, however, aroused suspicion that they may have a rather limited stability in the face of rainfall. Therefore samples were partially immersed into an excess of stirred distilled water at room temperature and visually monitored as a function of time. Within 2 days samples changed their color, which in a first step can qualitatively attributed to a decrease of the film refractive index. After prolonged exposure, the films began to delaminate in part. In Fig. 1, the photograph of a typical specimen is shown as observed after 64 h. Areas with both-sided MgF_2 coating coexist with sections where the film is removed either from one or the two sides. In regions close to the shearing edges, where the water is agitated due to stirring, areas even above the nominal surface line are delaminated. This debonding is delayed by careful sample handling (slow withdrawal, cautious rinsing) but cannot completely avoided after extended exposure.

On first view, this damage caused by water at room temperature seems to contradict the film stability during steady-state testing [9] at 85 C at 85% relative humidity. In part, the observation can be explained by the fact that the

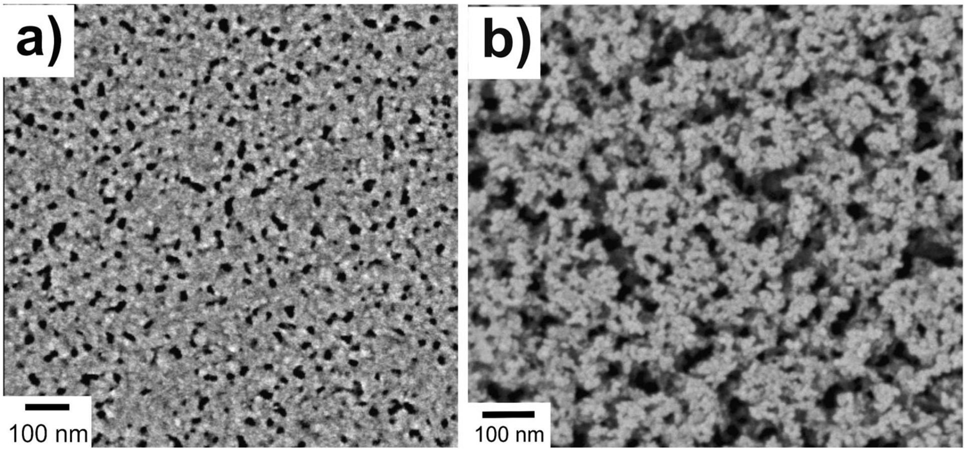

Fig. 2 Surface view SEM images of **a** as-prepared MgF_2 films on borosilicate glass and **b** after 64 h exposure to water

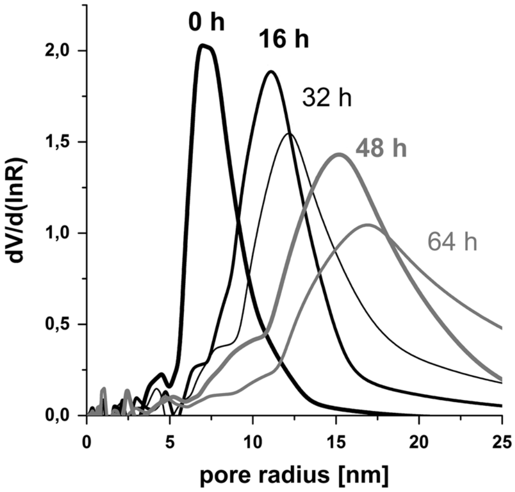

Fig. 3 Pore size distributions of MgF_2 films on borosilicate glass as determined by EP. The samples have been exposed to a water bath for the times indicated

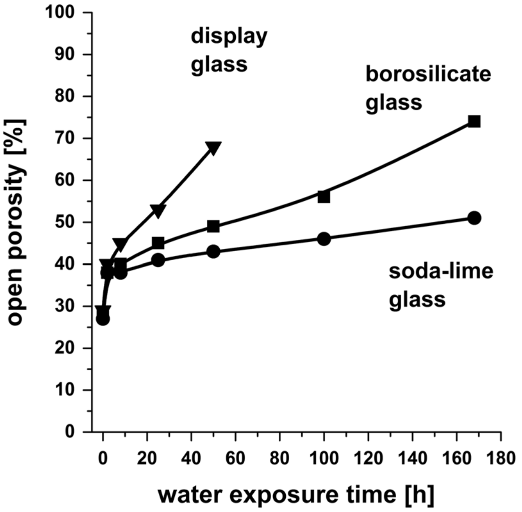

Fig. 4 Open porosity of MgF_2 films deposited on different glass substrates after exposure to a water bath as determined by EP

solubility of MgF_2 lessens with temperature [13]. Furthermore it has to be taken into account that during 85/85 testing, there is no liquid water phase present that can remove dissolved MgF_2 from the films by diffusion.

In Fig. 2a, the SEM surface image of an as-prepared MgF_2 AR coating is given. The fine-grained porous structure looks homogeneous, the size of the pores is in the order of magnitude of the MgF_2 particles. After 64 h exposure to water, larger voids become apparent (Fig. 2b). It seems as if larger aggregates of interconnected primary particles detached from the film surface. It is reasonable to assume that any dissolution process will weaken the inter-particle contacts and that after prolonged water exposure some of these links will break and adjacent grains still joined will be removed. As this will also happen at the particle-substrate interfaces, large film segments may debond as seen in Fig. 1.

The increase in pore size as suggested by Fig. 2b can be quantified by EP. Whereas for as-prepared MgF_2 films the maximum of the pore size distribution is about 7 nm, this value rises with exposure time to water. Additionally the pore size distribution broadens as one would expect as the consequence of detachment of particulate aggregates. (Fig. 3)

Using different substrates, significant alterations regarding film dissolution and detachment were observed. In Fig. 4, the open porosity of MgF_2 films deposited on different glass types is given as a function of exposure time to water. Using sodium-free display glass, the steepest increase in porosity is detected; after 50 h the MgF_2 films are fully delaminated. Material deposited on borosilicate glass exhibits a higher stability whereas best results are observed on soda-lime glass. This sequence suggests that sodium ions from the substrate may lead to an improved strength of the MgF_2 material.

In order to support this hypothesis, XPS depth profiles of layers on borosilicate and soda-lime glass with film

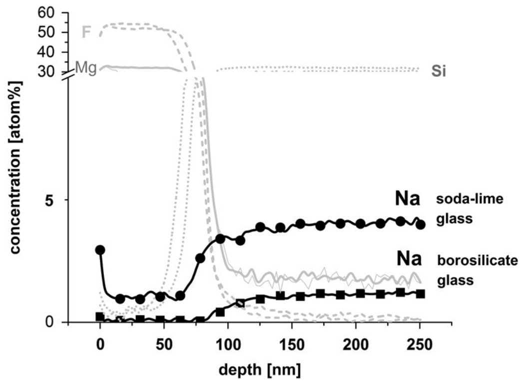

Fig. 5 XPS depth profile of MgF_2 films prepared on soda-lime and borosilicate glass

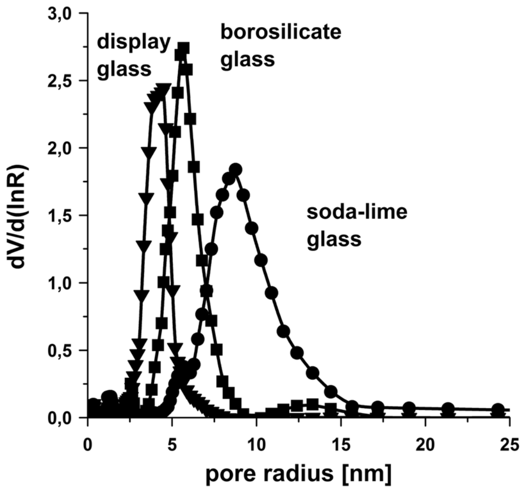

Fig. 6 Pore size distributions of MgF_2 films on different substrates as determined by EP

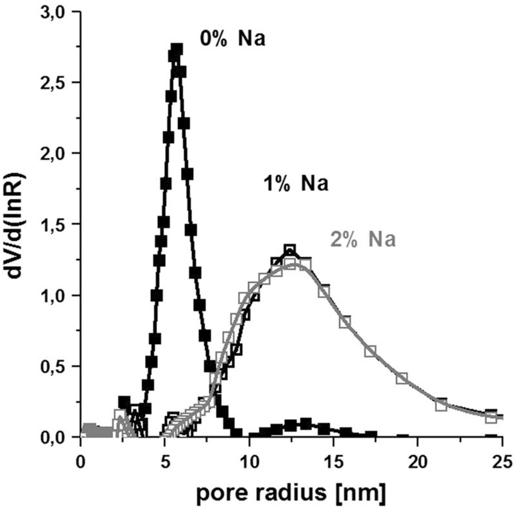

Fig. 7 Pore size distributions of MgF_2 films on borosilicate glass containing 0% (undoped), 1 and 2% sodium

thickness' of approximately 110 nm were measured. The results are shown in Fig. 5. The outcomes regarding Mg, F and Si are comparable. The borosilicate substrate shows a lower Na content as one would expect from the glass composition, only minor amounts of sodium diffuse into the MgF_2 film during thermal treatment. In contrast to that, a significant level of Na ions is found in the MgF_2 coating on soda-lime glass.

Since with 42.2 g/l, the solubility of NaF in water is significantly higher than that of MgF_2 (0.13 g/l) the stabilization of MgF_2 by the incorporation of sodium ions into the film backbone may be envisioned at first sight. Beyond that, the structural features of the films may be altered due to the presence of sodium. In Fig. 6, the pore size distributions of as-prepared MgF_2 films on the different substrates are displayed. There is a qualitative relationship between substrate sodium content and pore size. Given a comparable initial porosity (Fig. 4), smaller pore sizes are associated with smaller particles and thus an enhanced specific surface. It is reasonable to assume that material dissolution is facilitated from higher surface areas. Based on the present data, the possible stabilizing effect of Na incorporation into the MgF_2 backbone and improved microstructural features pointing in the same direction cannot be separated from each other.

The doping of film material by effusion from the glass is far from being reproducible, furthermore applying thicker films may result in sodium concentration gradients. In order to circumvent these problems and to allow stable films on low-sodium substrates, Na was introduced into MgF_2 coating solutions as a dopant. In Fig. 7, the pore radius distribution of an undoped film (0% Na) on borosilicate glass is compared to samples employing 1 and 2 mol% sodium with respect to the Mg content. Due to the Na, the maximum is shifted from 6 nm to approximately 13 nm, the radius distribution is broadened significantly. The doping level of 1% seems to be sufficient since no further alteration for higher Na contents is observed.

Comparing these results with Fig. 5, the "intrinsic" doping affects the microstructure of the films more than the Na effusion from soda-lime glass, even though comparable final Na concentrations (~1% in Fig. 5) are established.

As can be seen from Fig. 8, doping has a benign effect on the stability of MgF_2 films vs. dissolution/delamination in water: compared to sodium-free coatings doped systems only show a moderate increase of porosity, delamination is prevented for exposure times exceeding 10 days.

4 Conclusions

The presence of sodium, either originating by effusion from glass substrates or introduced as dopant to coating solutions,

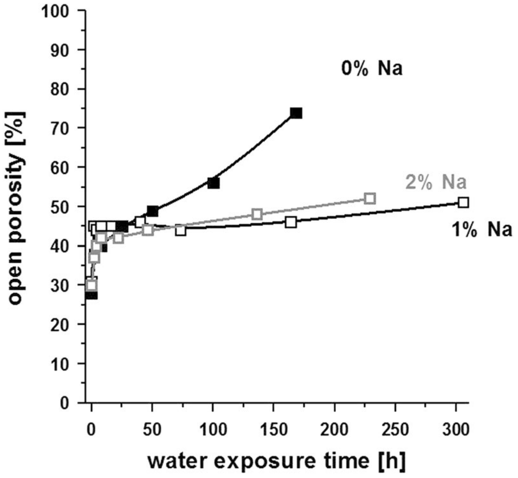

Fig. 8 Open porosity of MgF_2 films on borosilicate glass prepared from solutions containing 0, 1 and 2% sodium as dopant after exposure to a water bath

has a pronounced effect on the microstructure and solubility of sol-gel derived MgF_2 films.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interests.

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