Moisture retention influence on the anti-reflection properties of magnetron sputtered Low-E coating stacks with ZnSnO\(_x\) top layers

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Abstract. The influence on the optical properties of AR Low-E PVD coatings with silver IR-reflectors on glass substrates from the water absorption into their outer ZnSnO\(_x\) dielectric layers was considered with the use of VIS/NIR-spectrophotometry. The estimations of coatings absorption shift reversibility depending on the initial contact with water duration as well as of the mechanisms responsible for the changes in optical constants of the stack’s layers, supported with the comparative analysis of experimental and modelled spectra, are reported. It was shown that the water vapour sorption within the top zinc stannate layer leads to the shift in optical qualities of the whole stack by the changes in the stack’s absorption spectrum in the visible range. This effect proved to be reversible with the water exclusion via the samples heat treatment, but only until the water diffusion into the depth of the Low-E stack reaches the Ag layers, propagating the aggregation, that can no longer be cured with the temperature impact. The change in integral visible-range absorption reaches up to \(\Delta A_{\text{vis}} = 0.5-1\) abs.\% in comparison to the “as-deposited” samples, suggesting that the presented observations can be employed for VIS/NIR-spectrophotometry of such coatings for the purpose of their initial wetting determination, as well as the control of their further degradation.

1. Introduction

Anti-reflective (AR) coatings are widely used nowadays, deposited onto the surfaces of various optical components with the purpose of decreasing reflection and correspondingly increasing the optical transmission through them. They are used in production of various lenses for optical instruments and eye-glasses, cover glasses for photovoltaic modules, in windows and various electronic devices manufacturing [1-3]. The AR-effect is traditionally achieved via the destructive interference in the beams reflected from the interfaces of the coating layerstacks, and constructive interference in the corresponding transmitted beams. In the most simplistic case of the single-layer AR coating deposited onto the transparent substrate, the optimum AR effect is achieved for the given wavelength \(\lambda\) according to the Fresnel’s law with the layer thickness of \(\lambda/4\), and it’s refractive index equal to the square root of those of the substrate [4].

The principles of AR-effect found also a particular application in production of low-emissivity (Low-E) coatings on the large-scale format flat glass for architectural and transport glazing.
applications. Such coatings contain layers that effectively reflect IR-radiation – typically of either silver or gold - which reduce irradiative heat losses, as well as protect the interiors from external solar thermal impact [5, 6]. These metallic IR-reflecting layers within the Low-E coating stacks have a relatively high refractive index and are surrounded by the auxiliary dielectric layers. These dielectric films together with the IR-reflectors form an anti-reflective coating group and serve for additional compensation of the absorption of visible light as it passes through the metal layers. Modern Low-E coatings consist of over 7 individual layers of different materials and thicknesses with alternating high and low refractive indices, due to which they are characterized by low reflection losses in the entire visible spectral range [7-10].

In [11], it was shown that the reversible absorption of moisture by the external porous SiO$_2$ layer of the AR coating led to a noticeable increase in the coating’s effective refractive index thus leading in its place to a well-resolved decrease of the AR-properties effectiveness. It was demonstrated that even the VIS-only spectrophotometry of such coatings with a top SiO$_2$ antireflection layer can serve as a reliable mean to detect the fact of “wetting” of the coating at the initial stages of the process and can be therefore employed as an alternative to FTIR spectrometry [11-14].

As an alternative to silica-oxide another material widely used as an external dielectric layer of Low-E stacks is the tin doped (stannate) zinc oxide - ZnSnO$_x$ [6, 15-17]. There is no information in it's regards however on the possibility of water absorption determination possibility (including the early stages of “wetting” process) via the VIS/NIR-spectrophotometry, as well as on this process reversibility.

The aim of this work is to study the influence of water absorption into the external dielectric ZnSnO$_x$ layers of anti-reflective stacks of PVD Low-E glass coatings on their optical properties, as well as the reversibility of this process.

2. Experimental

Experiments on the thin films deposition were performed on an industrial magnetron PVD line VonArdenne GC330H for large-size architectural glass coating. Soda-lime float glass plates with the thickness of 6mm and the format of 2250*3640 mm coated with a Low-E thin film stack SunCool-R Bronze 45/25 ProT (according to technical requirements bulletin TU 23.11.12-003-59354526) served as a substrate for deposition. ZnSnO$_x$ was deposited as an external layer in relation to the whole AR part of the stack in all of the experiments. The resulting AR group of thin films looked as follows: glass substrate – the first spectral widening dielectric (SiNx) – silver absorber – top ZnSnO$_x$ dielectric. The depositions of the Low-E stack and the top ZnSnO$_x$ layer were performed in a single “vacuum” stage without bringing the samples out to the atmosphere until the completion of the whole thin film structure. No heating was applied towards the glass substrate during the deposition of any of the layers.

Zinc stannate depositions were performed during a reactive sputtering process while sputtering metallic targets with magnetron plasma of mixed Ar+O$_2$ atmosphere of working gases. During these depositions the position on the reactive material sputtering hysteresis has been maintained with the help of optical control of characteristic emissions from plasma with an automatic loop adjustment of required reactive gas component flow. The Ar flow was approximately 650 scem in all of the experiments, and flow amounts for both of the gas components were controlled by MKS mass flow controllers. The total resulting gas pressure in the chamber was maintained at the level of approximately 4.5×10$^{-3}$ mbar respectively.

The sputter targets were made of binary ZnSn (50wt% Sn) alloy. The minimal purity for the alloys used was 99.7% with the alloy concentration stability of ±2 wt.%. A dual rotating cylindrical magnetron system, driven by a TRUMPF Hüttinger TruPlasma power supply, installed in the line chamber was used for sputtering. It operated in pulsed DC mode at the frequency of 33 kHz and the power limit of 65±4 kW.

The ZnSnO$_x$ layer thickness was (14±1) nm in all of the experiments. It was established and then maintained at the given range via indirect control based on the spectrophotometric ex-situ
measurement in the range of wavelengths between 350 and 1300 nm. Spectra were obtained in transmission and film-side reflection from the samples. Elemental analysis of the surface features of the coatings was performed using the SEM/EDS with a VEGA3 Tescan microscope equipped with Oxford Instruments Xplore EDS module. Spectrophotometry was made in the transmission and reflection modes using a PerkinElmer Lambda 950 UV/VIS/IR spectrophotometer with a 90 mm integrating sphere operated in a wavelengths range 250-1000 nm. Bruker FastScan AFM with a silicon nitride cantilever (silicon tip ~1nm in diameter) operated in peak force taping mode was used to determine the topography of the coatings.

3. Results and Discussion
AFM analyses demonstrates that the surfaces of the deposited films have a porous structure and consist of very fine rounded grains with a lateral size of about 16-20 nm in diameter (Fig. 1).

Figure 1. AFM surface morphology analysis (height sensor image).

After the deposition the samples were kept in a tank filled with DI water with a conductivity $\sigma$ maintained at 2 $\mu$S and a temperature of 40 °C for the periods of various durations. The samples have been annealed after their exposure to water in a muffle furnace at a temperature of 650 °C for 8 minutes each. Comparative spectrophotometry was performed on the samples after the steps of water tank bathing and heat treatment accordingly.

As a result of the first hour of water tank “bathing” a decrease in coating’s absorption intensity was observed in the range of 350-400 nm along with a corresponding increase in the range of 450-750 nm and further equalization with the initial spectrum curve obtained straight after the deposition closer to the IR-border (Fig. 2-A). This optical behavior on the early stages of wetting is seemingly related to the absorption of water into the porous surface of ZnSnO$_x$ coating layer directly. That leads to the layer’s effective refractive index $n$ increase, which is proved also by the direct ellysometric measurements performed on the mono-layered zinc-tin-oxide glass coating samples similarly exposed to water at the wavelength of 632 nm (Fig. 3). This change in refractive index value of the top layer of the anti-reflection layerstack group leads correspondingly to the according shift in the resulting AR-properties of the whole thin film structure.

This assumption was proved with the modeling of the spectral properties of the according coatings in CODE VP software package. Several optical models were constructed in which the top ZnSnO$_x$ layer of the thin film stack was successively replaced by a water-containing layer of increasing thickness with corresponding refractive index and extinction coefficient. This approach was aimed at simulating the diffusion of H$^+$ and OH$^-$ ions into the depth of the thin film with continuous water sorption. One can see that the behavior of the modeled absorption spectra corresponds well to the results of experimental measurements (Fig. 2-B).
Figure 2. Absorption spectra behavior in: (A) – experiments of “bathing” the samples in a DI water tank; (B) – modeling the absorption of water into the external ZnSnO layer; (C) – annealing the samples preliminary exposed to water. Durations of exposition of samples to water (A,C) and the depth of the modeled water diffusion into the external layer of the stack (B) are stated in figures.

Figure 3. Results of elipsometric measurement of the ZnSnO coating on glass refractive index as a function of sample exposure to water duration.
The further shift in absorption spectra with keeping the samples in contact with water is characterized by the general absorption intensity increase throughout the whole measured wavelengths range in comparison to the spectra of those of the samples that have been exposed to water for up to a one hour (Fig. 2-A). The spectra for the longer water exposition durations still feature the negative absorption intensity deviation in 350-400 nm range and on the contrary it’s positive deviation in 450-750 nm in comparison to the behavior of the curve measured on the as-deposited sample. These changes in the absorption spectra seem to be due to the diffusion of H⁺ and OH⁻ ions deeper into the thin film stack structure in direction of the Ag layer. Once the aqueous radicals reach the interface of the silver layer, the former is caused to degrade in process of aggregation from a homogeneous film into the form of individual crystallites. Such effects and the mechanism described are well known from the literature [18-21]. As a confirmation of their potential taking place in the given case, the presence of foci of silver layer aggregation can be resolved on the EDS elemental maps of the surface of the coatings that have been exposed to water for a considerable amount of time within the set of experiments performed (Fig.4).

Reversibility of the observed optical effects caused by water retention within the group of AR layers of a Low-E thin films stack was studied with the spectrophotometry of the samples preliminary bathed in a water tank after their further annealing in a muffle furnace at the temperature of 650° C for 8 min. each. According to the results of this study the absorption spectra of those of the samples that have been exposed to water for longer then 1 hour showed an increase of deviation from the base-spectrum of the as-deposited sampe within the whole visible range. At the same time this deviation has decreased for those of the samples, for which the water tank bathing duration was less (Fig. 1-C). Based on these observations one can conclude the general reversibility of changes in AR-qualities of Low-E thin films stacks that take place during the absorption of water in their top ZnSnOₓ layer. Upon the further diffusion of retained water into the depth of the layerstack an effect of degradation of the light transmission of the coating however occurs due to the corresponding silver layer aggregation. This effect is irreversible and remains even at the annealing of the samples.

4. Conclusion

Based on the results obtained, it can be concluded that the optical properties of the antireflective stacks of Low-E PVD coatings on glass in the visible range are affected by the absorption of water into the external dielectric ZnSnOₓ layers of the stacks. The observed drift in AR properties of the
antireflection thin film groups within Low-E layerstacks that occurs during the absorption of water into the external ZnSnO_x layer is proved to be reversible with the aqueous components desorption, propagated by annealing of the samples. The effect of the coating’s light transmission decrease due to the aggregation of the silver layer upon further diffusion of the trapped water deeper into the layerstack structure, however, persists during annealing of the samples. This result can be used for VIS/NIR spectrophotometry of such silver-based low-emissivity glass coatings with an external dielectric ZnSnO_x layers in order to establish the fact of their initial wetting and to control their further degradation.

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