Oleophobic optical coating deposited by magnetron PVD

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Abstract. Thin oxinitride films of Zn-Sn-O-N and Si-Al-O-N were deposited on glass by reactive magnetron sputtering at various nitrogen-to-oxygen ratios. Nitrogen added to oxygen led to decrease of the surface roughness and increase of oleophobic properties studied by the oil-drop test. The best oleophobity was obtained for Zn-Sn-O-N oxinitride at Zn:Sn=1:1 and N:O=1:2. Improved oleophobic properties were also demonstrated if the oxinitride film was deposited on top of the multilayer coating as the final step in the industrial cycle of production of energy efficient glass.

1. Introduction

Sputter deposited thin films are widely used in production of architectural flat glass [1]. These coatings consist of 3 to 40 layers of various materials mainly of metals and metal oxides. The thickness of individual layers is in the range of several to hundred nanometers [2]. The energy efficient glasses, for example, consist of a sequence of dielectric and silver layers, where thin (~10 nm) silver layers reflect infrared radiation back into the room, while dielectric layers protect the silver from chemical and mechanical degradation and are anti-reflecting [3]. All the layers are usually deposited by magnetron sputtering, which is a standard coating technology for large-area flat substrates [4-7].

A common problem of these energy-efficient coatings is their wear damage and surface fouling due to deposition of non- or hardly-removable oily and suety contaminations. This may happen due to contact with liquids for glass-cutters, transport rollers, dirty protective gloves, bare hands, etc.

To overcome this problem, considerable efforts have been undertaken to develop a technology of the oleophobic surface. Surface oleophobity states for the surface tension to repel oils and viscous liquids. It leads to a diverse array of applications including self-cleaning, stain-free cloth and drag reduction. It is known that oleophobic properties are improved if the surface is uniformly nanostructured and the surface curvature of its elements is big. Such surface structure has large contact angles with viscous liquids (above 150 degrees) and small contact angle hysteresis. Materials free of pores and cavities, which could act as nanocapillars, demonstrate a better oleophobity [8]. The methods used for oleophobic processing are: electrospinning, liquid vapor deposition and spray atomization [8-10]. They however cannot be applied to thin layers.

The purpose of this study is to analyze the possibility of improving oleophobic properties of thin films in application to energy-efficient transparent conductive multilayer coatings on glass substrates.
The process must be easily incorporated in the technological cycle of PVD magnetron coating and must not affect negatively the properties of the main functional coating.

The dielectric materials mainly used as the top layers of transparent conductive energy-efficient coating on glasses are two-component metal oxides where metals are from the group: Ti, Si, Zn, Sn, In, Zr, Al, Cr, Nb, Mo, Hf, Ta, and W. The oxides are good barriers against oxygen diffusion and withstand mechanical stresses [2] thus preventing chemical degradation, cracking, and exfoliation. The surface of the outer oxide layer needs protection against oily contaminations.

It was observed, that introduction of nitrogen as a second gas component along with oxygen during sputter deposition favors formation of a more dense and uniform nanostructurized surface structure with high surface curvature of its elements [11]. Therefore, oxinitrides seem to be promising from the point of view of improving oleophobity. Two metal compounds for oxinitriding were selected: Zn-Sn and Si-Al, as the respective oxide layers are often used in multilayer optical coatings on architectural glasses [12-16].

2. Experimental
Deposition of protective coatings was performed in an industrial line VonArdenne GC330H for coating of architectural glass with dimensions of 4×6 m. This line is used for multi-layer deposition of metals and metal oxides. Full-scale soda-lime glass sheets 4 mm thick were used for deposition. The sheets were cleaned according to a standard technological procedure before film deposition. This procedure was a sequence of cleaning in deionized water and drying using compressed dry air. Films of zinc-stannate oxinitride Zn-Sn-O-N, and aluminum doped silica oxinitride Si-Al-O-N were physically deposited by reactive magnetron sputtering directly on bare glass substrates without intermediate layers. Glass sheets were not heated during deposition.

After experiments with bare glass sheets, the optimal oleophobic coating was also deposited on top of the multilayer energy-efficient industrial glass product by adding an extra step of oxinitride layer deposition to the standard technological chain.

Targets for sputtering were made of respective bi-metal alloys. Two Zn-Sn targets with various alloy compositions were used: one with 50 wt.% Sn (±2 wt.%) and another with 10 wt.% Sn (±2 wt.%). The Si-Al had 10 wt.% Al (±2 wt.%). The minimal purity of all the metals was 99.7%. Dual rotating cylindrical magnetron system, driven by a TRUMPF Hüttner TruPlasma power supply was used. The power supply operated in pulsed DC mode at the frequency of 37 kHz and the power of 50 to 52 kW.

The amount of gases introduced into the sputtering chambers was controlled by the MKS mass flow controllers. Reactive sputtering has been performed in the mixture of argon, oxygen, and nitrogen. Argon was used as the sputter component, while oxygen and nitrogen were reactive components. Nitrogen flow varied from 0 to 800 sccm. Oxygen flow was set to sputter the targets in the transition mode of material poisoning hysteresis and for all the used materials was at the average of 800 sccm. The argon flow was set to keep the total pressure of the mixed gases at the level of approximately 3.5×10⁻³ mbar.

Comparison of the oleophobic properties was made by the so-called “oil-drop test”. A small drop (0.5±0.1 ml) of a given viscosity was applied on the surface, and its diameter was measured in optical stereomicroscope. The drop diameter on the surface is directly proportional to the dip contact angle on the liquid/solid interface and characterizes oleophobicity. The larger the diameter of the drop spread over the surface, the worse the oleophobic properties of the surface with respect to the liquid of given viscosity. Three liquids of different viscosity were used for testing: immersion oil for optical microscopy with the viscosity \( V = 100-120 \text{ mPa·s} (T = 20°C)\), synthetic vacuum oil with \( V = 60-70 \text{ mPa·s} (T = 20°C)\), and liquid for glass-cutters with \( V = 20-40 \text{ mPa·s} (T = 20°C)\). In some cases the drop was round in shape and small in diameter, the contact angle was large, and this is the case of good oleophobicity. In other cases the drop spread over the surface, its boundary was noncircular, the contact angle was small, and this is the case of bad oleophobicity.
3. Results and Discussion
Results of the drop tests are shown in figure 1 for different test liquids. The diameter of the drop depends on viscosity of the test liquid and on the amount of nitrogen added to oxygen in the plasma-forming gas. In all cases nitrogen improves oleophobic properties of the surface.

The diameter of the drop as a function of the nitrogen flow demonstrates prominent decrease at the nitrogen flow rate above 200 sccm and has a minimum at around 350 sccm for all samples and all test liquids, which states for approximately a half of the oxygen flow (N:O=1:2). The rise of the diameter after the minima is rather slow.

The quantitative effect of nitrogen on oleophobicity depends on the surface and test liquid used. Liquids with low viscosity are less sensitive to oleophobic treatment, while the effect is rather high for liquids with high viscosity. For example the radius decreases about 3 times in the case of oil with $V = 60-70$ mPa·s on Zn-Sn-O-N (at Zn:Sn=1:1). The best oleophobic result was demonstrated by oxinitride Zn-Sn-O-N with equal weight ratio of components in the Zn-Sn sputter target (Zn:Sn=1:1).

Figure 1. Results of the "oil-drop" tests of three protection coatings and three liquids of different viscosity: $V = 20-40$ mPa·s (a); $V = 60-70$ mPa·s (b); $V = 100-120$ mPa·s (c). Solid line Si-Al-O-N (10 wt.% Al), broken line Zn-Sn-O-N (50 wt.% Sn), dotted line Zn-Sn-O-N (10 wt.% Sn).
Examples of SEM images of surfaces of Zn-Sn-O and Zn-Sn-O-N (50 wt.% Sn both) is given in figure 2. Oxinitride films in comparison with pure oxides have a smoother surface. There are no cavities on the surface of oxinitride films, which can work as capillars and accumulate viscous liquids making it difficult to remove them.

![SEM images of surfaces of Zn-Sn-O (50% wt Sn) deposited by reactive sputtering in pure oxygen(a) and Zn-Sn-O-N deposited if 500 sccm N2 was added to oxygen (b).](image)

**Figure 2.** SEM images of surfaces of Zn-Sn-O (50% wt Sn) deposited by reactive sputtering in pure oxygen(a) and Zn-Sn-O-N deposited if 500 sccm N2 was added to oxygen (b).

Dimensions of crystals in the film depend on many factors. One may suggest that oxygen and nitrogen compete during deposition of the film, giving increase in variety and the number of precipitates of oxide, nitride, and oxinitride phases. Oleophobic properties are linked with dimensions of nanocrystals. The best oleophobic properties were obtained if the flow rates of nitrogen and that of oxygen were 1:2 respectively, and if the concentrations of metals in the film were about 50:50. One can speculate that maximal concentration of phase precipitates and minimal crystal dimensions are expected in these conditions.

The oleophobic layer with optimal properties Zn-Sn-O-N (Zn:Sn=1:1 and N:O=1:2) was then deposited as the top layer on the industrial multilayer energy-efficient glass sheet as a final stage of the single technological process. Its thickness was chosen to ensure that all the initial product spectral properties remained the same. Standard quality control tests used on the production line did not show any issues with chemomechanical sustainability after deposition of the additional oleophobic top layer to the standard layer stack.

The standard glass with a multilayer coating and the test glass with additional oleophobic layer were tested with respect to oil fouling. Glass cutting oil was spilled over coated glass, and in some areas the oil was smeared into the surface by dirty gloves. The surfaces were dried, and then brush-washed using the standard procedure in the industrial glass washing machine. After washing there were no traces of oil on the oleophobic surface, while the surface without oleophobic layer retained a lot of oil. The procedure of washing of the standard glass was repeated several times with increase of pressure on the washing brushes. It was found that sticking of the oil to the standard glass surface was so high that deposited layers were destroyed and partially removed before oil was washed out. Figure 3 shows two surfaces after washing: the oil-free surface with oleophobic layer after the very first washing and the oil-fouled surface without oleophobic layer after many cycles of washing. One can see obvious damage of the standard layer-stack, which happened before the oil had been completely removed.
4. Conclusion

It was demonstrated that layers of oxynitrides Zn-Sn-O-N and Si-Al-O-N, which were deposited either on the glass surface directly or on the multilayer metal-dielectric stack on glass, both have prominent oleophobic properties. The oxinitrides have much smoother surface, which is possibly connected with nanocrystalline nature of the coating. The best result for Zn-Sn-O-N was obtained at Zn:Sn=1:1 and N:O=1:2, possibly because these conditions are preferential for nanocrystalline grain growth due to maximizing variety and number of phase precipitates.

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