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Novel GIMS technique for deposition of colored Ti/TiO_2 coatings on industrial scale

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The aim of the present paper has been to verify the effectiveness and usefulness of a novel deposition process named GIMS (Gas Injection Magnetron Sputtering) used for the first time for deposition of Ti/TiO_2 coatings on large area glass substrates covered in the condition of industrial scale production. The Ti/TiO_2 coatings were deposited in an industrial system utilizing a set of linear magnetrons with the length of 2400 mm each for covering the 2000 × 3000 mm glasses. Taking into account the specific course of the GIMS (multipoint gas injection along the magnetron length) and the scale of the industrial facility, the optical coating uniformity was the most important goal to check. The experiments on Ti/TiO_2 coatings deposited by the use of GIMS were conducted on substrates in the form of glass plates located at the key points along the magnetrons and intentionally non-heated during any stage of the process. Measurements of the coatings properties showed that the thickness and optical uniformity of the 150 nm thick coatings deposited by GIMS in the industrial facility (the thickness differences on the large plates with 2000 mm width did not exceed 20 nm) is fully acceptable form the point of view of expected applications e.g. for architectural glazing.

Keywords: *GIMS – Gas Injection Magnetron Sputtering; Plasma Surface Engineering; Impulse Plasma Deposition*

1. Introduction

In 2010, Zdunek et al. [1] proposed a new variant of plasma surface engineering process, namely a control of the plasma process through the use of pulsed, periodically variable concentration of working gas in the range of threshold values of about of 10^{-3} to 10^{-1} Pa. The idea of the process is as follows [2]: while the electrodes are permanently polarized, the discharge (for example the glow discharge in case of magnetron sputtering) could be cyclically initiated and then vanished accordingly with the pressure pulses with a given frequency. As the pressure fluctuations in the threshold range, taking place in the interelectrode space, have in such conditions extremely dynamic oscillatory character, an average value of the pressure at which the glow discharge exists is much lower than at the standard conditions especially during the continuous gas flow described well by the Pashen curve. The dynamics of the discharge which is developing under condition of pressure pulsation in the threshold range increases the plasma instabilities and, in turn, makes the plasma to be far from the equilibrium. A higher free path of the gas (plasma) should result in a smaller loss of kinetic energy of particles on mutual collisions due to increased free path of the particles in comparison to the standard condition for magnetron sputtering. One of the most spectacular effects of the solution is that

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the coatings become denser with very good adhesion to the substrates, even in non-heating condition during the deposition process.

The idea of gas mode control in the plasma processes has been positively proved in practice firstly for the IPD technique (Impulse Plasma Deposition) [3–7] and next for the pulse magnetron sputtering deposition (PMS) (e.g. [8–11]); we named the "gas" modified PMS as the GIMS (Gas Injection Magnetron Sputtering) [7, 12]. The use of gas mode for deposition of TiN coatings on non-heated cutting tools by the modified IPD method enabled 16-fold increase of the tools lifetime in comparison to the uncoated tools [1]. This is a substantial improvement compared with 2 to 4 times extending of the coated tools service life that was previously reported in literature for tools coated in industrial scale production with the use of regular, not modified IPD method (especially the IPD with continuous flow of the working gas under the pressure of about of 10 to 20 Pa) [13, 14] and for tools or machine parts coated with the use of other plasma methods described in the literature (e.g. [15–19]). Another example of the advantage of using gas mode control in the plasma surface engineering can be found in our recent research regarding the use of GIMS and PMS techniques for deposition of TiO_2 coatings on unheated glass or silicon substrates [20]. It has been shown that GIMS leads to a synthesis of rutile TiO_2 films, while in case of using PMS an anatase phase dominates. Taking into account that typically the rutile coatings are deposited only on heated or/and the electrically polarized substrates (otherwise the anatase films are produced, e.g. [21]), our results presented in the literature [20] seem to prove the mentioned above assumption that compared to PMS, the "gas controlled" technique provides more kinetic energy to the plasma particles which play an active role during the film nucleation phase.

Lately, Skowronski et. al. [22] have proposed an interesting variant of producing colored coatings deposited by the GIMS technology on glass substrates by the use of two thin layers Ti/TiO_2 colored coatings. In the system, the 300 nm thick Ti layers played a role of a reflective undercoat while the color of the coating was the result of the light interference taking place in the area of transparent TiO_2 layer deposited on the Ti undercoat.

The aim of the present paper was to verify the effectiveness and usefulness of the novel GIMS for deposition of Ti/TiO_2 coatings on large area glass substrates covered in the condition of industrial scale production. The uniformity of the colored Ti/TiO_2 coatings deposited in such condition was the main requirement for commercial application of the coatings, e.g. for architectural glazing.

2. Materials and methods

2.1. Coatings deposition technology

The Ti/TiO_2 coatings were deposited at the industrial facility in the BOHAMET Company, Poland utilizing a set of linear magnetrons with the length of 2400 mm each, for covering the 2000 × 3000 mm glasses. This facility was described previously in the literature [22]. Fig. 1 presents the view of the industrial line made of four vacuum chambers with a total volume of 24 m^3. The deposition section of the facility has been equipped with a set of three linear magnetrons with the length of 2400 mm each, enabling subsequent deposition of three different groups of coatings (in unreactive or reactive mode with the use of three different target materials). In our experiments only one of those magnetron was used. The Ti (grade 1) target was used and the deposition was conducted in Ar and in a $Ar+O_2$ (1:4) mixture correspondingly for production of Ti and TiO_2 layers. According to the GIMS technology [2, 7, 12, 17] the working gas was periodically injected with a controlled frequency of an order of 10 Hz to the interelectrode space by a set of pulse bistable valves maintaining the pressure in the range of an order of 10^{-3} to 10^{-1} Pa. The magnetron was permanently supplied by a DPS supplier working at a power of 24 kW in the unipolar PMS mode at a base frequency of 100 kHz with 2 kHz modulation. Glass plates of dimensions about 30 × 30 × 5 mm each were placed in the crucial points along the magnetron length accordingly to the individual gas injection outlets (Fig. 2). The substrates

were degreased using a commercial solution based on a mixture of alcohols and surfactants. Plasma cleaning of the substrates was performed in the first section of the apparatus just before the deposition process. The substrates were not intentionally heated during the layers deposition. Three types of layers were deposited: pure metallic Ti layer only, transparent TiO_2 layer deposited directly on the glass substrates and the color bilayer Ti/TiO_2 coating. The Ti films were deposited under a pulsing pressure with an average value of 0.06 Pa in the Ar plasma during the period of time of 260 s, while the TiO_2 films were deposited on titanium coated glass as well as directly on glass substrates under the pulsing pressure of the A+O_2 mixture with an average value of 0.25 Pa, under the period of time of about of 350 up to 1000 s.

Fig. 1. Industrial facility for large area glasses covering built up and working at BOHAMET Company. The facility was used in the present work.

2.2. Coatings properties characterization

The samples were examined by means of spectroscopic ellipsometry, spectrophotometry and confocal optical microscopy. Additionally, the metallic films were investigated using four probe method. The thickness of Ti films was determined from a linear interface layer/substrate profile applying a confocal optical microscope Lext OLS 4000 from Olympus. In turn, the thickness of dielectric films was estimated from ellipsometric measurements. The reflectance and transmittance were measured in the wavelength range of 200 nm to 800 nm for near-normal incidence of light, applying a Cary 5000 (Agilent) spectrophotometer. The surface resistivity of metallic films was determined by the four probe from Jandel Engineering, Ltd.

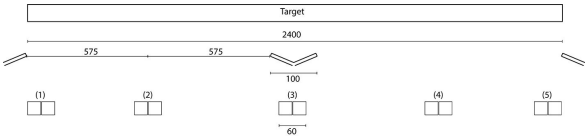

Fig. 2. Specimens location along the magnetron cathode. The numbered (1 – 5) positions were specially chosen, taking into account the essential points with respect to the gas outlets (all of the dimensions are given in mm).

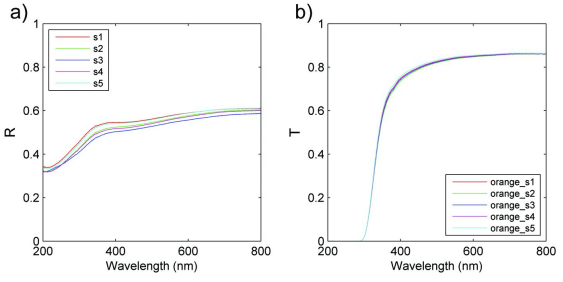

Fig. 3. Reflectance spectra for Ti samples (a) and transmittance spectra of transparent TiO_2 layers (b).

3. Results and discussion

In contrast to the standard magnetron sputtering processes with continuous gas flow in the GIMS, the pressure was pulsed in the threshold limit of values at which the glow discharge was initiated and vanished periodically. As it was mentioned before the crucial goal of the experiments was to check the uniformity of the optically sensitive coatings deposited under the GIMS conditions exploited in an industrial scale facility. According to the results reported in the literature [23] we were sure that the presently produced layers in the argon/oxide mixture atmosphere were made from TiO_2. Table 1 collects the thickness and resistance measurement results of the obtained layers.

Fig. 3 and Fig. 4 present some chosen optical properties of the coatings.

Table 1. Thickness and resistivity of the layers positioned along the target length.

Layer type/position of specimen		1	2	3	4	5
Ti	Thickness, nm	131	152	150	149	141
	Resistance, Ohm	13.48	11.55	13.01	11.53	11.41
TiO_2 on glass	Thickness, nm	18.50	19.10	18.10	18.30	18.60
		26.70	28.10	26.50	26.40	26.90
		51.30	56.40	54.00	53.50	53.20
TiO_2 on Ti/glass	Thickness, nm	16.40	17.00	16.30	16.10	15.60
		24.80	26.00	24.70	24.60	23.90
		49.30	51.80	51.00	49.80	48.30

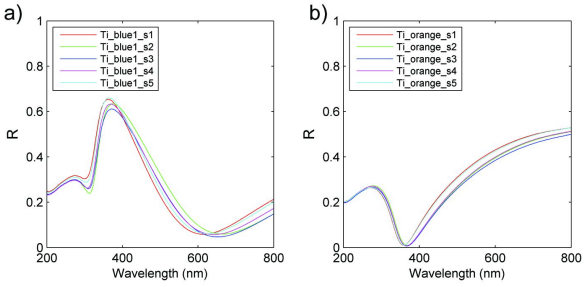

Fig. 4. Reflectance spectra of the colored TiO_2/Ti/glass coatings for the thinner (a) and thicker (b) titanium oxide layers.

All the measurements performed in our experiments have shown that the differences in the layers properties were in the range of few percent of measured value. The achieved result is slightly worse than that reported in the work [23] for a similar industrial installation where the standard Gemini PMS system, powered by a continuous flow of the working gas, was used. It should be noted, however, that – in that case – magnetrons had a length of 750 mm instead of 2400 mm as in the device used by us. According to our studies we are convinced that the GIMS technology is suitable for deposition of Ti/TiO_2 coatings on large area glass substrates in industrial scale.

4. Conclusions

The main aim of our study was to verify the effectiveness of GIMS technology to produce color layers built up on the basis of two layers in bilayer system coatings of titanium and titanium oxide. The color effect in these layers is obtained only by the light interference taking place in a very thin region with the thickness of about 20 to 50 nm of titanium oxide layer deposited on titanium undercoat. Taking into account the specific features of GIMS technology, resulting from dynamic changes of pressure in the critical range and the size of the device (linear magnetron with a length of 2400 mm for production of optical layers on the glass of 2000 × 3000 mm), the key issue was to investigate the optical homogeneity of the produced layers. Our research has shown that fluctuations of the essential properties of thin layers having a thickness of tens of nanometer did not exceed a few percent on the length of 2400 mm which is an acceptable result from production point of view.

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