DIFFUSE COPLANAR SURFACE BARRIER DISCHARGE PRE-TREATMENT FOR IMPROVING COATING PROPERTIES

Tomáš HOMOLA, Vilma BURŠÍKOVÁ, Pavel SŤAHEL, Mirko ČERNÁK

Masaryk University, Department of Physical Electronics, Kotlářská 2, 611 37 Brno, Czech Republic

Abstrakt

Diffuse Coplanar Surface Barrier Discharge (DCSBD) was used to pre-treat surfaces of glass in order to remove adsorbed carbon contaminants and increase surface energy due to incorporation of oxygen-based polar functional groups. Afterwards, the plasma pre-treated glass surfaces were coated with TiO_2 film deposited from sol-gel solution. Tribology measurements in coatings showed significant increase of adhesion of coatings deposited onto pre-treated surfaces, whereas coatings deposited onto untreated surfaces showed poor adhesion. Increase in adhesion is related with both cleaning and formation of functional groups. Cleaning, or removal of adsorbed carbon contaminants, led to uniform coating without any areas of surface energy instabilities, whereas functional groups provided necessary bonding between coating and surface.

Klíčová slova: atmospheric plasma, plasma treatment, sol-gel, adhesion

1. INTRODUCTION

Unique mechanical and optical properties designate glass for a use in numerous applications in several sectors of industry. Nearly always, the glass surfaces are being coated by protective or functional layers to enhance their properties. Application of coatings sometimes meets difficulties when adhesion of the coating on glass substrate is not adequate. This is mostly due to lack of functional groups or high amount of contaminants on glass surfaces. For example, organic contamination encourages the formation of electrostatic faults, such as dielectric breakdown of the deposited films onto glass in LCD's [1]. Surface contaminants may also produce spots of non-homogeneity in coatings, resulting in rapid quality decrease of optical coating for instance.

Recently, the atmospheric pressure plasma showed as an efficient tool for removing of organic contaminants as well as incorporation of functional groups onto treated surfaces [2], [3]. Atmospheric pressure plasma for surface treatments is more preferred than low pressure plasma, because it could be easily up-scaled for industrial needs, and the plasma-chemical processes are often faster and more efficient. In this work, a coplanar dielectric barrier discharge (DBD) was used to treated glass samples to improve their surface properties before application of functional TiO_2 coating. Then the coating was studied by scratch tester to determine the influence of treated surface on coating quality and indentation equipment to estimate hardness.

2. EXPERIMENTAL

2.1 Materials and plasma treatment

The Diffuse Coplanar Surface Barrier Discharge (DCSBD) system (Roplass s.r.o., Czech Republic – www.roplass.cz) is made from multiple parallel strip-like molybdenum electrodes, embedded in 96% alumina. The dimensions of alumina ceramic of the DCSBD system are 93 cm in width and 230 cm in height and the total area of plasma is approximately 80 mm × 200 mm. The DCSBD plasma consist of numerous H-shaped luminous micro-discharges [4] that can be either static or traveling on a dielectric surface along embedded strip electrode, their density varying from a single to many micro-discharge events produced per AC halfcycle [5]. The DCSBD micro-discharges are generated differently than those in volume DBD. Whereas common volume DBD generates filamentary micro-discharges orientated perpendicularly to treated surface, the DCSBD produces micro-discharges parallel to treated surface [6]. Moreover, filamentary part of surface micro-discharges can be supressed when glass surface is introduced to the plasma as a treated substrate, which was reported in our previous study [7]. Furthermore, total suppression of filamentary plasma occurs when glass coated with thin indium-tin oxide coating is introduced to the plasma, which represents a unique method for generation of diffuse plasma in ambient air [8].

In this study flat soda-lime glass samples (Marienfeld GmbH, Germany), of 26 mm × 76 mm × 1 mm dimension, were treated by atmospheric air plasma generated by (DCSBD) for 5 s. Then, the samples were coated by TiO_2 from sol-gel by dip-coating method at speed 300 mm/min. After dip-coating process, the samples were dried in oven at 50 °C for 1 hour. The thickness of the coating was approximately 0.7 µm. For mechanical properties analysis, five samples were prepared: one reference (bare glass substrate), two untreated samples and two plasma treated samples. Plasma treatment was performed in dynamic mode [7] for 5 second. Plasma treatment method is detailed described elsewhere [7].

2.2 Surface analyses

The TiO_2 coating quality was examined by scratch tester Revetest Xpress plus (CSM Instruments). The progressive scratch tests were carried out with linear increase of the scratch load from 1 N to 71 N. The scratch line length and the loading rate were 18 mm and 80 N/min, respectively. As an indenter, Rockwell diamond with radius of 200 µm was used.

Fischerscope H100 instrumented indentation tester equipped with diamond Berkovich indenter was used to study the indentation resistance of the samples. Several indentation loads were applied in the range from 5 to 500 mN to obtain the depth dependence of the hardness and elastic modulus of the coating-substrate system. This method enabled to study not only the mechanical properties of the TiO_2 coating but also the indentation resistance of the coating-substrate interface.

3. RESULTS AND DISCUSSION

The untreated and plasma treated glass samples were coated with TiO_2. The samples were investigated by scratch tester and obtained results are summarized in Table 1. We observed critical load for creation of first cracks (Lc1) at approx. 9 N and 15 N for untreated and plasma treated glass surfaces, respectively. The intensive cracking (Lc2) of the TiO_2 coating occurred at the load of approx. 17 N and 28 N for untreated and plasma treated glass surfaces, respectively. Partial delamination of the coating in the scratch path (Lc3) was observed at the load approx. 40 N for the coating on untreated glass surface. On the other hand, coating on the plasma treated glass showed no partial delamination in the scratch path. Intensive chipping of the glass (Lc4), i.e. damages to glass bulk, were observed approx. at the load 54 N and 66 N for coating on untreated and plasma treated surfaces, respectively. The higher values of critical loads for coating of plasma treated glass surfaces show higher quality and higher adhesion of the coating on glass surface, which is due to plasma interaction with surface before coating process. The DCSBD plasma treatment leads to removal of organic contaminants adsorbed from ambient environment, and moreover to "activation" of surface, i.e. incorporation of polar groups [7]. The observed effect of higher coating quality on plasma treated surface is therefore due to higher concentration of reactive groups on glass surface that can contribute into bonding between coating and glass. Also lower carbon concentration on plasma treated glass surfaces [7] might be critical for adhesion. The uncoated glass surface and TiO_2 coating on untreated glass surface show similar Lc4 (the cracking in the glass bulk) about 54 N. The coating on glass surface treated by plasma has higher limit for bulk damages at 66 N, therefore the plasma treatment clearly generates protective properties of the coating.

Sample	Lc1 [N]	Lc2 [N]	Lc3 [N]	Lc4 [N]
Reference (glass substrate)	9 ± 1	12 ± 2	-	54 ± 2
TiO_2 on untreated glass 1	10 ± 1	18 ± 3	43 ± 4	53 ± 4
TiO_2 on untreated glass 2	9 ± 2	16 ± 3	38 ± 5	55 ± 4
TiO_2 on plasma treated glass 1	15 ± 2	29 ± 2	-	66 ± 4
TiO_2 on plasma treated glass 2	16 ± 2	28 ± 2	-	59 ± 4

Table 1 Summary of the results from the scratch tests performed on TiO_2 coatings. Legend: Lc1 - critical load for creation of first cracks; Lc2 - intensive cracking; Lc3 - partial delamination of the coating in the scratch path; Lc4 - intensive chipping of glass.

We have also examined hardness (H) of the coatings on untreated and plasma treated glass surfaces. The results shown in Fig. 01 indicated an increase of hardness for coating deposited on plasma treated glass at indentation depths >500 nm. Although the measured errors for untreated and treated samples are overlapping, the trend in hardness difference is obvious for all measurements at indentation depth >500 nm, when the indentation depth is approaching the coating-substrate interface. This fact supports our conclusions made on the basis of the scratch test results that the coating quality in case of plasma treated substrates increased due to the increased coating-substrate interface resistance. The results of Young modulus measurements (not shown here) were also in good agreement with our findings. The presented results on hardness measurement indicated influence of plasma treatment on coating-substrate interface strength. Due to relatively high experimental error, the measurements should be repeated in the future with higher amount of samples treated for various times in plasma.

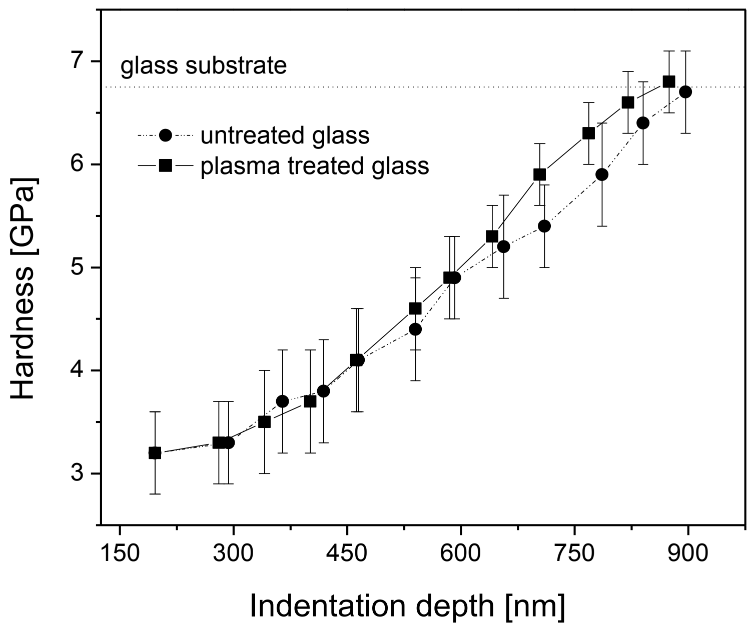

Fig. 01 Hardness dependence on indentation depth for TiO_2 on untreated glass and plasma treated glass.

ACKNOWLEDGEMENT

This work was supported by the program "Employment of Newly Graduated Doctors of Science for Scientific Excellence" (CZ.1.07/2.3.00/30.009) co-financed from European Social Fund and the state budget of the Czech Republic and by the project R&D center for low-cost plasma and nanotechnology surface modifications CZ.1.05/2.1.00/03.0086 funding by European Development Fund.

REFERENCES

[1] TAKAHASHI, H., K. SATO, S. SAKATA and T. OKADA *Charge leakage characteristic of glass substrate for liquid crystal display* 1,* J Electrostat (1995) **35** (4) 309.

[2] KORMUNDA, M., T. HOMOLA, J. MATOUŠEK, D. KOVÁČIK, M. ČERNÁK and J. PAVLÍK *Surface analysis of poly(ethylene naphthalate) (PEN) films treated at atmospheric pressure using diffuse coplanar surface barrier discharge in air and in nitrogen,* Polym Degrad Stabil (2012) **97** 547.

[3] HOMOLA, T., J. MATOUŠEK, B. HERGELOVÁ, M. KORMUNDA, L. Y. WU and M. ČERNÁK *Activation of poly(ethylene terephthalate) surfaces by atmospheric pressure plasma,* Polym Degrad Stabil (2012) **97** (11) 2249.

[4] ČERNÁK, M., Ľ. ČERNÁKOVÁ, I. HUDEC, D. KOVÁČIK and A. ZAHORANOVÁ *Diffuse Coplanar Surface Barrier Discharge and its applications for in-line processing of low-added-value materials,* Eur Phys J-Appl Phys (2009) **47** (2) 22806.

[5] ŠIMOR, M., J. RÁHEĽ, P. VOJTEK, M. ČERNÁK and A. BRABLEC *Atmospheric-pressure diffuse coplanar surface discharge for surface treatments,* Appl Phys Lett (2002) **81** (15) 2716.

[6] HODER, T., M. ŠÍRA, K. V. KOZLOV and H. E. WAGNER *Investigation of the coplanar barrier discharge in synthetic air at atmospheric pressure by cross-correlation spectroscopy,* J Phys D Appl Phys (2008) **41** (3) 035212.

[7] HOMOLA, T., J. MATOUŠEK, M. KORMUNDA, L. Y. L. WU and M. ČERNÁK *Plasma Treatment of Glass Surfaces Using Diffuse Coplanar Surface Barrier Discharge in Ambient Air (1),* Plasma Chem Plasma P (2013) **33** (5) 881.

[8] HOMOLA, T., J. MATOUŠEK, V. MEDVECKÁ, A. ZAHORANOVÁ, M. KORMUNDA and D. KOVÁČIK et al *Atmospheric pressure diffuse plasma in ambient air for ITO surface cleaning,* Appl Surf Sci (2012) **258** 7135.