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NANOSTRUCTURED LAYERS DEPOSITION FOR SELF-CLEANING GLASS

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Abstract: *This paper evidences research results on a new technology for deposition of* TiO_2 *nanostructured layers on glass. Air pollution, industrialization and everyday life activities are factors that point towards the need for efficient and ergonomic cleaning process of the impressive glazing surfaces that surround people in modern offices, leisure places and not the least, in houses. The design of equipment, the innovative technique based on pneumatically spraying a suspension of* TiO_2 *nanocrystals, the process parameters and preliminary test results for the obtained layers stand as main topics for the article. Integration of the system into industry 4.0 virtual intelligent platform is also presented. Further research development in order to validate the nanostructured* TiO_2 *coating on glazed surfaces is aimed.*

Key words: *nanostructured,* TiO_2 *layer, self-cleaning glass, deposition equipment, virtual intelligent platform.*

1. INTRODUCTION

Air pollution represents serious threat to the environment and personal health. The high increase of cars number, the drought for periods of several months followed by heavy rains and, not least, the excessive crowding of urban areas because of too many office buildings and blocks of flats, generate the need to find solutions which will contribute to reducing the effects of pollution on people's lives.

Correlated to the mentioned above, there is the need of good cleaning activities of offices, at home and in large public spaces such as concert halls, stadiums, etc. One focus is that of cleaning their windows and all other glazed surfaces efficiently and effectively.

There are famous producers of self-cleaning glass worldwide: GLAS EXPERT [1] that sells EVOCLEAN; VALRAS PROD SRL, [2] selling Clearshield; Saint-Gobain Glass [3] with BIOCLEAN [4] and, not the least, PILKINGTON [5].

Leading manufacturer of self-cleaning glass, Pilkington has introduced the Pilkington Activ™ (Japan) product range. This is the first dual-function glass, self-cleaning and reflecting the IR component of the solar spectrum. The advantage of Pilkington Activ™ coatings is that of using natural factors to keep the glass clean and it is based on action of the UV light that dissociates the organic molecules of the dirt layer so that, further, the raindrops do remove from the glass surface the dissociated organic layer.

One new technology for obtaining self-cleaning glass is based on hydrophilic titanium dioxide (TiO_2) coatings. This material has excellent photocatalytic properties, transparency over 85% in the visible spectral range, good chemical stability and high reflective index. The economic advantage of titanium dioxide is given by the abundance of titanium in nature but also by its low synthesis temperatures [6]. In addition, titanium dioxide exhibits antibacterial properties [7] which gives the possibility to manufacture glazed surfaces with dual effect, self-cleaning and antibacterial.

This paper presents research results on new technology for deposition of TiO_2 nanostructured layers on glass.

2. NANOSTRUCTURED LAYERS DEPOSITION

The new technology for nanocrystalline TiO_2 layers deposition is based an in-house developed and patented method [8]. The technique used is a simple, versatile method capable of generating controllable and reproducible complex nanostructures with various surface topology [9]. Moreover, the method is compatible with large area in-flow low-cost fabrication procedures. The ultrathin layers of approximately 400 nm thickness were obtained by pneumatically spraying a suspension of TiO_2 nanocrystals. The morphology of the layer is characterized by the reticulated appearance with craters of diameters ranging from 1.9 to 37 µm and depths of 0.2 to 1.3 µm (see Figure 1). Line profile of the crater marked with blue

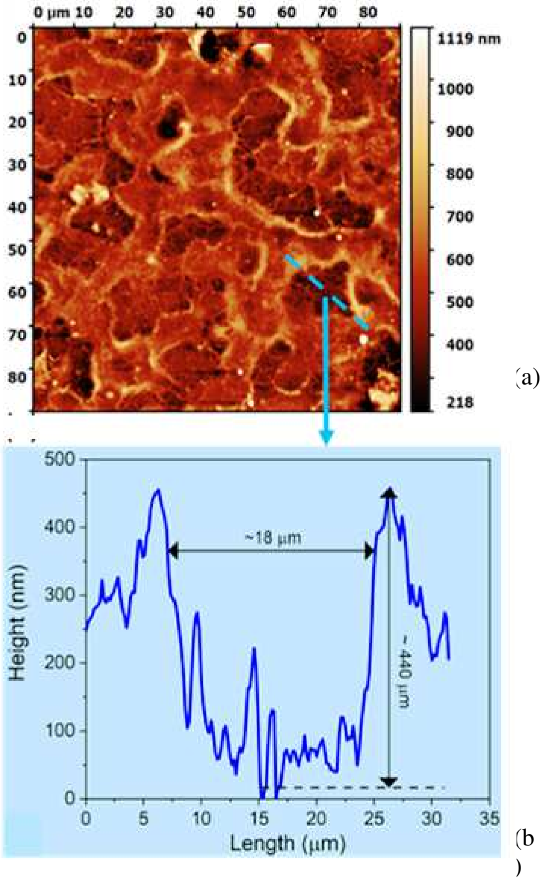


Fig.1. Typical AFM image for nanocrystalline TIO_2 layers; scanned surface 90 µm x 90 µm, the color bar in nm indicates height values (a); line profile of a crater marked with blue (b)

Through this innovative manufacturing process, the morphology of the TiO_2 layer can be modified for the benefit of the surface wetting properties and therefore, the self-cleaning efficiency. More of it, in order to obtain the finished product, TiO_2 films do not require long-term thermal treatments or, high temperatures. Practically, the maximum treatment temperature could be around 250 °C and the treatment time about 30 minutes.

In order to obtain samples (functional model) of glass (glazed surface) with nanostructured layers, the customized input data of are as follows:

- cutting to size the silico-calco-sodium glass surface with a thickness of 4 mm;
- washing the glass with detergent and warm water;
- ultrasonication in distilled water and isopropyl alcohol, in 3-5 successive stages;
- spraying the precursor substance for TiO_2 by Lechler pneumatic nozzle, with nitrogen carrier gas 5.0 at pressure of 2 kgf/cm^2;
- the distance between the spray nozzle and the substrate is 15 cm, the sweeping speed of the nozzle is 50 mm/s;
- the deposition temperature at which the substrate (glass) is maintained is 100°C, or 450°C (for these preliminary tests).

There were deposited films and bi-layers of TIO_2 (see Figure 2) under various conditions as mentioned next.

a. Compact TiO_2 films, referred to as P1, deposited at 450°C and had post-deposition thermal treatment at 450°C for 30 minutes.

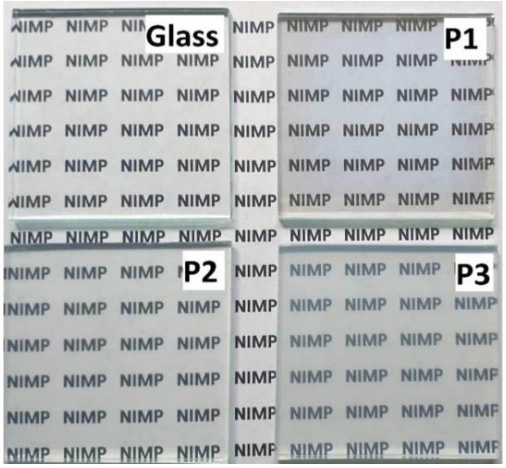


Fig.2. Samples for TiO_2 nanostructured layers

b. Mesoporous TiO_2 films, referred to as P2, were deposited at 100°C using a dispersion of TiO_2 nanoparticles and had post-deposition thermal treatment at 100°C for 10 minutes.

c. Bi-layers of mesoporous TiO_2/ compact TiO_2, referred to as P3. Mesoporous TiO_2 film was deposited at 100°C using a dispersion of TiO2 nanoparticles and post-deposition treated at 100°C for 10 minutes. Compact TiO_2 film was deposited at 450°C and underwent post-deposition thermal treatment at 450°C for 30 minutes.

Each of these obtained samples was evaluated from different perspectives, like: surface morphology, adherence to substrate and contact angle measurements.

The surface features were investigated by Atomic Force Microscopy (AFM) using a NT-MDTAuraNtegra Prima AFM system in noncontact mode.

The adherence to substrate of deposited layers represents a characteristic that will govern their quality and long-term sustainability. This adherence has been determined by the pull-off method (see Figure 3), according to ASTM D4541-22 - Standard test method for pull-off strength of coatings using portable adhesion testers.

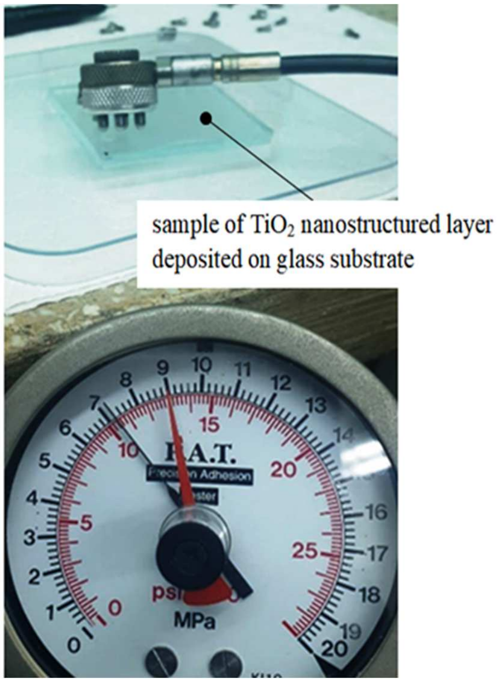


Fig.3. Setup for adherence tests

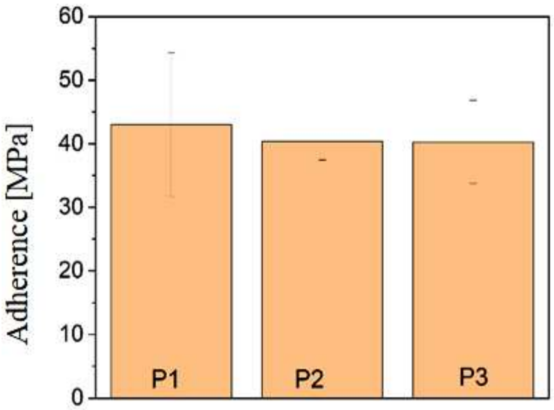


Fig.4. Average values obtained for each type of samples

The pull-off evaluation results indicated that the detachment of the nanostructured layers occurred every time at the layer-substrate interface, at values in the range of 37–43 MPa and that the failure is of adhesive type.

Statistical analysis (see Figure 4) indicated no significant differences between the other four types of TiO_2 deposited thin layers.

The hydrophobicity and / or hydrophilicity characteristics of the synthesized structures were investigated by static contact angle (CA) measurements.

The samples were positioned on a flat platform under the tip of a blunt-ended stainless steel needle with an outer diameter of 0.5 mm. The needle is attached to an automatically controlled syringe and used to drop controlled volume water onto the test surface as well as to assess the contact angle. The volume of the water droplets was about 1µl. For each individual sample, measurements were made at 5 different points on the surface.

The CA measurements were made by fitting the experimental profile of the droplet to second degree polynomial or, to circle equation. Then it was calculated the slope of the tangent to the droplet at the point of intersection with the line separating the liquid–solid - vapors interface. Example of the obtained results for the Glass and P1 samples is shown in Figure 5.

The experiments results could be summarized as: the smaller (and below 90°) value for the CA, the more hydrophilic the surface is.

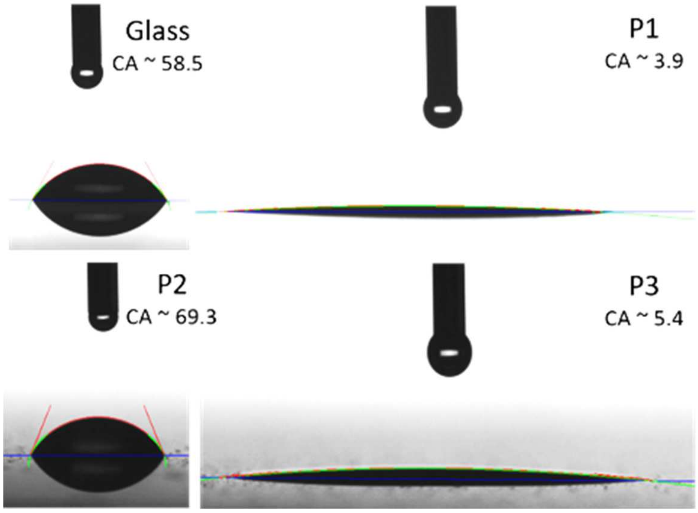


Fig.5. Values for the mean static contact angle for glass substrate, P1, P2 and P3 samples

3. EQUIPMENT CONCEPT AND MODEL

Previous research results mentioned in [10] present the design and prototype of a demonstrator equipment for the ultra-thin layers of solar cells with halogenated perovskites. There have been integrated three deposition techniques: screen printing, doctor blade and wire bar, each of them requiring customized condition for layers deposition.

This article evidence relevant aspect on the design and 3D model of the printing equipment designed for nanocrystalline TiO_2 layers deposition on glass surfaces.

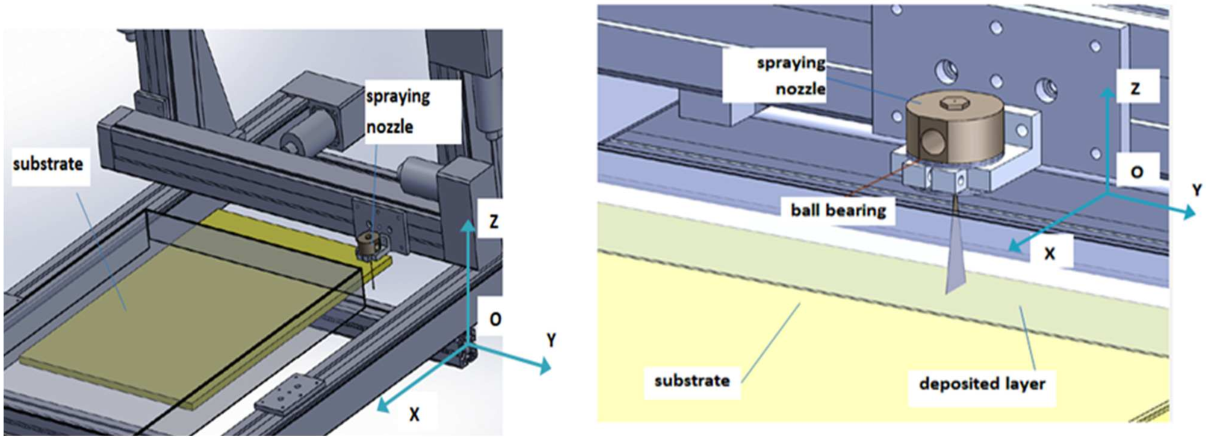
Based on experiments carried out on glass samples and their results (see chapter 2) the input condition for equipment concept are as follows next.

The structure is modular one, with distinct but interconnected modules:

- frame structure module;
- spraying system module;
- temperature module;
- operating system module;
- command and control module.

The motion types that the spraying nozzle subsystem must perform were set to be (see Figure 6) as mentioned next:

- motion along the OX axis, with a constant speed of approximately 10 m/min; the pitch being that of the lead screw, namely, 5 mm;
- motion along the OY axis, with different speed values within the interval [8 - 15 m/min];
- the distance from the head of the spray nozzle to the surface of the substrate, having different values, in the range [100 – 150 mm].



conic jet nozzle

linear jet nozzle

Fig.6. Model of the printing equipment

The case of using an ultrasonic nozzle that sprays a linear jet was also considered. For this hypothesis, nozzle inclination angles, relative to the OY axis, with values in the range (± 20°) will be considered. The inclination is to be possible due to ball bearing component mounted beneath the nozzle.

Some details on the modules and components are mentioned as follows (see Figure 7):

- the frame structure module is mainly made of Isel® extruded alloyed linear axes with ball screw (LES) aluminium profiles (PS) and;
- the spraying system module basically consists in pneumatic spraying nozzle;
- temperature module – is the one that ensures the required temperature for material deposition and is made of resistive resistances fixed in a thermal conductive plate;
- the operating system module is based on 5 servomotors with brakes;
- the command and control module is based on 5 axes controller.

There it can be also noticed the scheme for positioning the heat resistance beneath the equipment plate.

The basic scheme for the command and control system is shown in Figure 8. Design of the printing equipment, with subassemblies and components is shown in Figure 9.

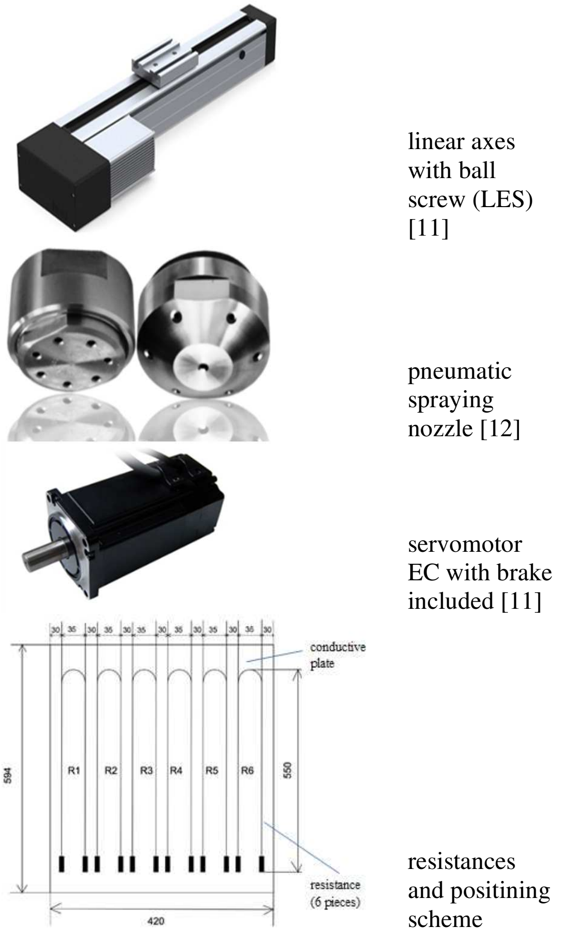


Fig.7. Printing equipment components

There it can be noticed the frame structure; the spraying system; the heating system for thermal treatment.

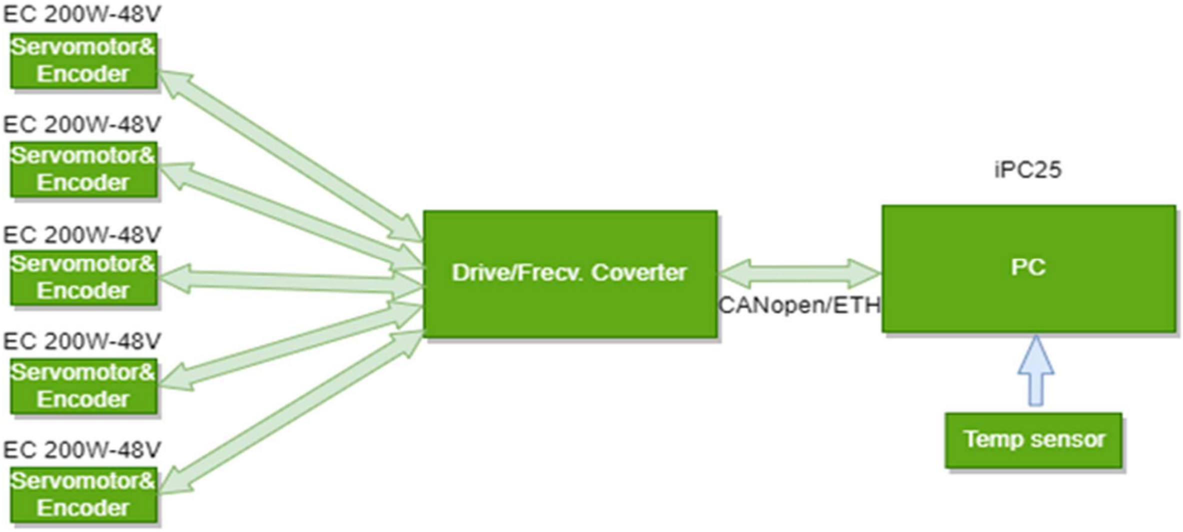


Fig.8. Command and control scheme

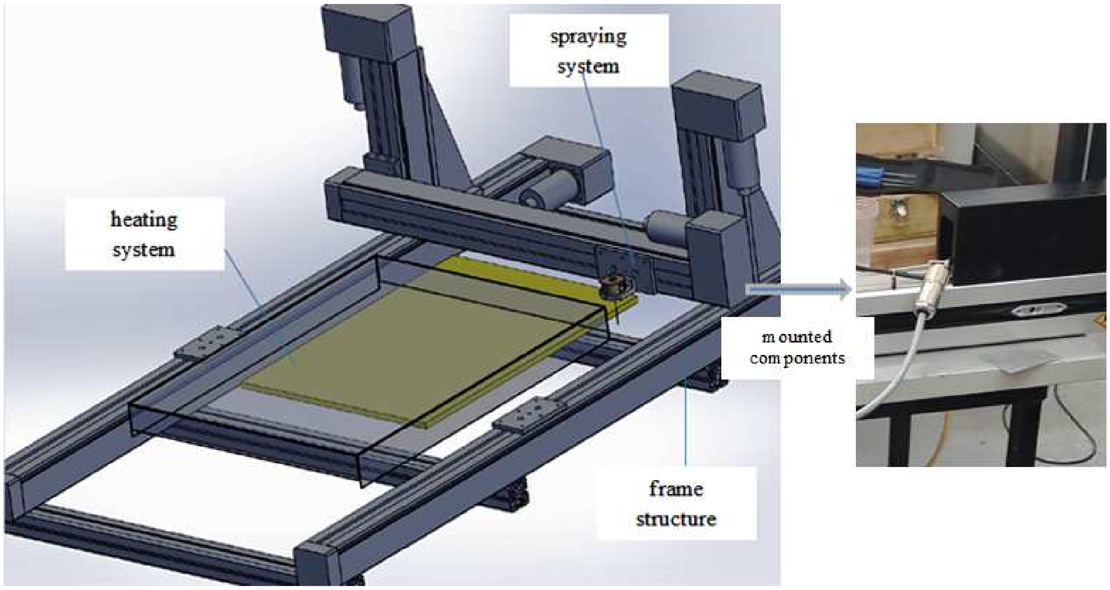


Fig.9. Drawing of the printing equipment

4. VIRTUAL INTELLIGENT PLATFORM

Integration of technology for obtaining nanostructured TiO_2 layers on glass, with self-cleaning and bacterial properties, into the industry 4.0 concept, is to be done by integration of the technological system into virtual intelligent platform.

To simulate the behavior of the system in different scenarios, its virtual model developed for ROS (Robot Operating System) and Gazebo is used. The system has three degrees of freedom, two degrees of freedom in the plane (XOY) and one degree of freedom along the OZ axis.

The motors for motions along each of the three axes motors are to be noticed (also) in Figure 10. There is (see also Figure 6) one servomotor that moves the nozzle along the OY axis, two servomotors that move the nozzle support along the OX axis and two servomotors that move the hole nozzle assembly along the OZ axis.

In order to run the simulations, the equipment CAD model (in Solidworks) is used and exported to perform dynamic experiments in the Gazebo work environment. Also, for model visualization and subsequent adjustments, the ROS module called RVIZ is used.

The physical properties of the model are described in a URDF (XML format) file which will be automatically generated by Solidworks after defining the system properties. This file describes the model's kinematics (joint position and orientation, end-effector) and dynamics such as mass, inertia, collision geometry, and visual appearance. The transmission and control of the joint are also descried in the file.

The position and orientation of the motion axes are considered relative to this coordinate system. All the constructive and dynamic elements of the CAD model have been exported for a precise motion simulation.

Based on the dynamic constraints of the constructive elements, the inertia matrix, gravity, friction forces, etc. were defined.

The three axes are controlled in the virtual environment by means of dedicated drivers, similar to those used on the physical system, which perform position control on the vertical axis and velocity control for the translational motions of the nozzle on the plane

Position and speed control interfaces are used to send and receive the commands for the controllers mentioned above.

Once the model is loaded in ROS, you can interact with it in the simulation environment. For the printing equipment system it is possible to: generate motions along each axis using *moveit* package, apply forces on different points, simulate limit sensors on the axes.

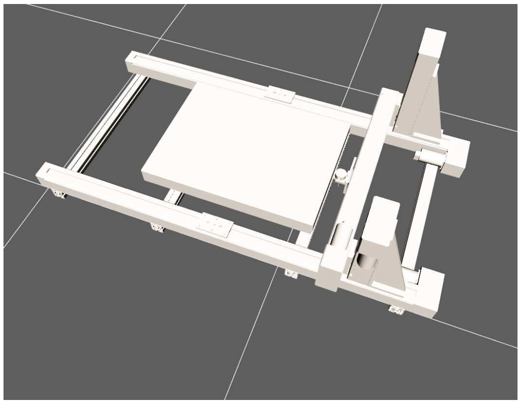


Fig.10. Rviz visualition of the model.

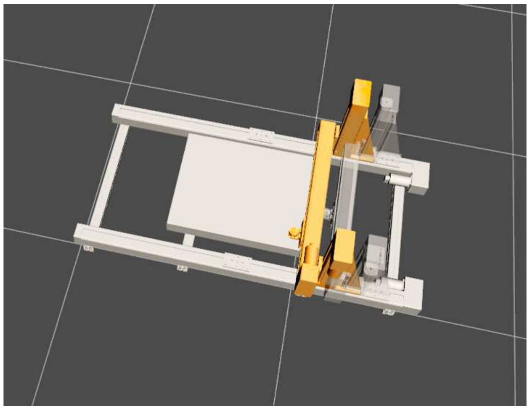


Fig.11. Virtual simulation of motions for spraying

For the realistic simulation the transmission in the axes of the system may also be taken into account.

Since for this equipment there are no gearboxes, differentials or other types of transmission mechanisms, the simulation will not assume such intermediate mechanisms.

Virtual simulation of the motions for TiO_2 nanocrystalline TiO_2 layers deposition has been done (see Figure 11), meaning linear motions along OX and OY axes. The motions of both parts were tested taking into account the linear limits of the system. The speed of the motors was set to constant using a PID controller. The test confirmed that there are no collisions between the moving parts of the printer.

5. CONCLUSION

TiO_2 layers showed a reticulated appearance, with pronounced unevenness of the order of tens of microns. Self-cleaning window coverings' adhesion to the substrate is a feature that will govern their quality and long-term sustainability. The pull-off evaluations indicated that the detachment of the TiO_2 layers occurred every time at the layer-substrate interface, at values in the range of 37–43 MPa.

The contact angle analyzes revealed that the P1 and P3 samples are super hydrophilic therefore the wettability of surface is increased, in report with bare glass and P2, which in turn will help the water droplet to spread over the dust and clean the surface by taking dirt with it.

The equipment design is to be fit to the requirement of the technological process for nanocrystalline TiO_2 layers deposition.

In order to simulate the behavior of the deposition system in virtual environment we are using ROS before deploying the model to the real one. The virtual simulations indicated that the prismatic links are moving without colliding with each other, while the nozzle is able to correctly spray the glass with the desired layers of TiO_2.

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Depunere de straturi nanostructurate pentru suprafețe vitrate cu proprietăți antibacteriene

Această lucrare evidențiază rezultatele cercetării privind o nouă tehnologie de depunere a straturilor nanostructurate de TiO_2 pe sticlă. Poluarea aerului, industrializarea și activitățile din viața de zi cu zi sunt factori care indică necesitatea unui proces de curățare eficient și ergonomic a suprafețelor vitrate impresionante care ne înconjoară în birourile moderne, locurile de agrement și nu în ultimul rând, în case. Proiectarea echipamentului, tehnica inovativă bazată pe pulverizarea pneumatică a suspensiei de nanocristale TiO_2, parametrii procesului și rezultatele testelor pentru straturile obținute reprezintă subiecte principale descrise în articol. Este prezentată și integrarea sistemului în platforma inteligentă virtuală, industrie 4.0. Se urmărește dezvoltarea ulterioară a cercetării pentru validarea acoperirilor nanostructurate cu TiO_2 pe suprafețele vitrate

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