SiO₂/TiO₂ multi-layered thin films with self-cleaning and enhanced optical properties

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Abstract. Self-cleaning, high transmittance glazing was obtained by cold spray deposition for glazings. The thin films contain TiO₂, SiO₂ and Au nanoparticles in different structures which allow for tailoring the optical, hydrophilic and photocatalytic properties. The crystallinity, morphology and surface energy were correlated with the optical transmittance and reflectance; the transmittance increased from 89.45 (for the glass substrate) to 91.76% when Au nanoparticles were used in the tandem layered structures. The samples containing alternating multi-layered SiO₂ and TiO₂ thin films without gold nanoparticles show hydrophilic surface; for these layers, the photocatalytic efficiency reaches 40% under simulated solar radiation. A conditioning effect based on adsorption was observed to increase the photocatalytic efficiency. These highly transparent coatings are well suited for glazings and fenestration, showing the self-cleaning effect based on combined superhydrophilicity and photocatalysis.

Keywords. SiO₂/TiO₂; multi-layered; cold spray deposition; optical properties; photocatalysis.

1. Introduction

Considering the European legal frame, by 2020, about 20% of the buildings energy consumption needs to be reduced, along with a similar decrease in the CO₂ emissions in order to significantly diminish the greenhouse gases effect. The main objective of these strategies consists of finding innovative solution to reduce the fossil fuels use, including the development of new ‘virtually zero-energy/nearly zero-energy buildings’ having as references for passive energy buildings [1].

Nowadays, solar–thermal systems represent some of the most important, market competitive solutions, designed for increasing the solar energy use in the thermal energy production; the key components in the low-temperature devices are the flat-plate solar–thermal collectors (FPSTC), largely used for domestic hot-water preparation, installed on roofs, terraces, facades, balconies, etc. [2]. Extending the share of energy produced using FPSTC asks for increasing the thermal output by developing efficient absorber plates, decreasing the losses, etc. [3]. Additionally, the implementation of FPSTC on facades and other highly exposed building parts has to answer to architectural constraints, thus, solar thermal collectors with optimized shape and colour need to be developed, while preserving the optical and thermal performances [3]. One of the most important path in increasing/preserving the initial efficiency is to allow solar radiation to reach the convertor (absorber plate) to a large extent, thus, to have a highly transparent glazing and to avoid its fouling during exploitation.

Based on these, recent studies outline the need for improving the optical properties of the glazing: high transmittance in the UV–Vis–NIR range, low UV–Vis reflectance, potential self-cleaning properties along with controlled wettability, by using alternating thin oxide layers. The common component in these stacks is silica, coupled with photocatalytic oxides.

Different techniques were used to obtain silica thin films such as plasma-enhanced chemical vapour deposition (PECVD) [4], plasma-assisted reactive magnetron sputtering (PARMS) [5] and atomic layer deposition (ALD) [6]. As flat-plate solar–thermal collectors have polymeric glazing, the high temperature thermal treatment of the thin films does not represent an option. Thus, low-temperature deposition techniques should be employed and/or thermally annealed powders should be further deposited at temperatures below 60°C.

Silica thin films are often reported as being obtained via sol–gel techniques, using various precursors, such as tetraethylorthosilicate and methacryloxypropyltrimethoxysilane, to get an increased glass substrate Vis transmittance at values >90% and reflectance values <10% [7]; it was observed that the lower refractive index of SiO₂ nanoporous thin films could increase the UV–Vis transmittance [8], adding >4.3% to the 85% threshold value [9].

Multi-layered thin films of SiO₂–TiO₂ with increased transmittance in the visible range and anti-reflective, were obtained by dip-coating the glass substrate, using sol–gel precursors [10]. The photocatalytic and self-cleaning properties of the SiO₂–TiO₂ composites (obtained from sol–gel powders) are reported as complementary to the increased transmittance

[11,12], outlining the role of crystallinity and controlled morphology [13,14]. Thin films of $\text{SiO}_2\text{--TiO}_2$ were also obtained by spin coating onto a glass substrate [15] and the highest transmittance composite film could also provide high wettability to the samples [16]; sputtering [17], chemical vapour deposition [18] and electrodeposition [19] are also reported to obtain multi-layered thin films of SiO_2 and TiO_2 .

Dip coating is a low-cost, easy to control technique, but it raises two main issues when targeting the development of the glazed cover in a flat-plate solar collector: (1) it is difficult to apply in thin layers with constant thickness on large surfaces (in a commercial collector, the glazing is of about $2. \dots 3 \text{ m}^2$); (2) it covers both sides of the glazing with identical layers; from a functional point of view, the inner and the outer sides of the glazing are subjected to very different conditions (wet, hot atmosphere on the inner side and atmospheric conditions on the outer side, with large temperature variation), thus, different wetting properties are expected for an efficient double-side effect.

Based on this analysis, the paper presents a novel approach to develop thin films of multi-layered oxides, with controlled optical and photocatalytic properties. To the best of our knowledge, there are no reports on $\text{SiO}_2\text{--TiO}_2$ multi-layered thin films with increased optical, hydrophilic and photocatalytic properties obtained by a simple and low cost technique: cold-spray deposition applied using dispersions of SiO_2 and TiO_2 nanoparticles. The paper reports the novel results obtained by optimizing the sol-gel SiO_2 preparation and the development of alternating thin layers of oxides for glazing in novel flat-plate solar-thermal collectors integrated in the built environment. The influence of the gold nanoparticles on the films' properties is also discussed, as contributing both to the morphology control and to the multiple reflection properties of the thin layers. Photocatalytic degradation of methylene blue (MB) is employed to outline the self-cleaning potential, able to remove organic mist deposited on the glazing.

2. Experimental

2.1 Powder preparation

Tetraethylorthosilicate (TEOS, 99.9%, Sigma-Aldrich), ethanol (EtOH, P.A.M Corporation SRL), HCl (37% concentration, Scharlau), and ultra-pure water (Direct-Q3 Water Purification System) were used to synthesize the SiO_2 gel, using a TEOS:EtOH:HCl:H₂O in 1:8:3:0.5 volume ratio. The as-prepared SiO_2 gel was then calcinated at 600°C for 2 h to obtain the SiO_2 powder.

The titanium powder used in this work was TiO_2 P25 Degussa (Evonik, a mixture of anatase and rutile in a 20:80 wt ratio).

The gold nanoparticles were prepared through microemulsion synthesis (provided by the Politehnica University of Bucharest as aqueous, $5 \mu\text{M}$ dispersion) [20].

The silica and titania dispersions were prepared by mixing 0.25 g SiO_2 powder in 50 ml ethanol:water (1:1 v/v), respectively, 0.05 g TiO_2 powder in 50 ml ethanol. These systems were ultrasonically dispersed for 9 min and then stirred for 5 min.

2.2 Thin films deposition

The $\text{SiO}_2\text{--TiO}_2$ multi-layered thin films were obtained by cold spray deposition on microscopic glass ($2.5 \times 2 \text{ cm}^2$), using a 6 axes robot (ABB, model IRB5400) with a control software (ABB, IRC5P control system) and a heating ceramic plate (Ceram, model HP1212M). The glass substrate was initially cleaned by ultra-sonication in alcohol and then dried using compressed air.

The multi-layered thin films were obtained by successive deposition; each layer was deposited in 3 sequences with a 5 min break between the sequences for SiO_2 and 10 min for TiO_2 , at 60°C , to allow the removal of the continuous medium. The carrier gas was compressed air, at 1 atm. To test the gold nanoparticles effect, different volumes of metal aqueous dispersion ($5 \mu\text{M}$) were added to the titanium dioxide dispersions, in concentrations of 350, respectively $1500 \mu\text{ l}^{-1}$. The samples code and the layers structures are presented in table 1.

2.3 Characterization

The crystalline and the amorphous phases of the multi-layered thin films were investigated by XRD, using a Bruker D8 Discover Advanced diffractometer with locked coupled continuous scan, a scintillation counter (12,800 steps, 2 s per step) and $\text{CuK}\alpha_1$ radiation ($1.5406 \text{ \AA}$ wavelength, at 40 kV, 20 mA).

The surface morphology was analysed using scanning electron microscope (SEM, Hitachi model S-3400 type 121 II) and atomic force microscopy (AFM/STM, NT-MDT model NTEGRA Probe Nano Laboratory). The images were taken in semi-contact mode with Si-tips (NSG10, force constant 0.15 N m^{-1} , tip radius 10 nm). The average roughness measurements and the porosity were evaluated using NOVA SPM software.

The surface elemental composition analysis of the films was performed by energy dispersive X-ray (EDS, Thermo).

Static contact angle measurements with the sessile drop method were measured using an OCA-20 Contact Anglemeter (Data Physics Instrument) to outline the wetting properties. The measurements were done with a maximum error of 0.5° for water on the metal oxide thin film and 0.3° when using glycerol and PEG as wetting liquids.

The Perkin Elmer UV-Vis-NIR spectrometer (Lambda 950 equipped with 150 mm integrating sphere) was used to investigate the optical properties and the thickness of the $\text{SiO}_2/\text{TiO}_2$ multi-layered thin films. Thickness values were calculated based on reflection spectra at 6° incidence angle.

Table 1. Samples code and the layers' structure of SiO₂/TiO₂ multi-layered thin films.

Samples' codes (no. of deposited layers)	The layers' structure	Concentration of gold nanoparticles ($\mu\text{mol l}^{-1}$)
SiO ₂ _3 (1)	Glass/SiO ₂	—
TiO ₂ _3 (1)	Glass/TiO ₂ (1)	—
TiO ₂ _350AuNP_3 (1)	Glass/TiO ₂ _350AuNP	350
TiO ₂ _1500AuNP_3 (1)	Glass/TiO ₂ _1500AuNP	1500
SiO ₂ _TiO ₂ _3_3 (3)	Glass/SiO ₂ /TiO ₂ /SiO ₂	—
SiO ₂ _TiO ₂ _350AuNP_3(3)	Glass/SiO ₂ /TiO ₂ _350AuNP/SiO ₂	350
SiO ₂ _TiO ₂ _1500AuNP_3 (3)	Glass/SiO ₂ /TiO ₂ _1500AuNP/SiO ₂	1500
SiO ₂ _TiO ₂ _3_5 (5)	Glass/SiO ₂ /TiO ₂ /SiO ₂ /TiO ₂ /SiO ₂	—

2.4 Photocatalytic experiments

The photodegradation experiments were done in a cylindrical homemade reactor using simulated solar radiation by using one F18 W/T8 black light tube (UVA, typically 340–400 nm, with max = 365 nm, flux intensity 3 lx, Philips) and two TL-D Super 80 18 W/865 lamps (Vis white cold light tubes, typically 400–700 nm, with max = 565 nm, flux intensity 28 lx, Philips), placed annular to the photoreactor.

The pollutant dye tested in this work was methylene blue (MB, C₁₆H₁₈N₃SCl, 99.8%, Merck). The pollutant solution was prepared using ultra pure water (Direct-Q3 Water Purification System) in a previously optimized concentration of 0.0125 mM (4 ppm) [21].

The photocatalytic efficiency of methylene blue was calculated using equation (1):

$$\eta = (c_0 - c)100/c_0, \quad (1)$$

where c_0 represents the initial concentration of the dye solution and c represents the dye's concentration after photodegradation, evaluated based on the calibration curve at the maximum absorption wavelength experimentally registered at $\lambda = 665$ nm [22].

3. Results and discussion

3.1 Crystalline structure

XRD data are presented in figure 1 for the SiO₂/TiO₂ multi-layered thin films deposited on microscopic glass. The diffractograms show a predominant amorphous structure that can be related to the sol–gel SiO₂, proving that the thermal treatment of the silica powder did not support crystallinity. The crystallinity percentage in the multi-layered films is about 18%, mainly due to the TiO₂ anatase polymorph. The lower percentage of crystallinity (17.6%) in the TiO₂_3 sample is influenced by two factors: the substrate (glass) background and the relative low thickness (45.3 nm) of the TiO₂ thin film.

Figure 1. XRD patterns of SiO₂–TiO₂ multi-layered thin films.

The crystallite size and crystallinity percentage were calculated using Diffrac.Suite EVA 5.14 dedicated software allowing to interpolate all the detected diffraction peaks in each sample. The theoretical thickness was calculated by the addition of SiO₂ and TiO₂ monolayer thicknesses (experimentally measured values) multiplied with the number of layers corresponding to each sample.

The crystallite sizes in table 2 are almost constant and show that the deposition did not significantly alter the initial Degussa P25 crystalline ordering; the addition of gold nanoparticles leads to smaller crystallites supporting the assumption of larger internal stress induced by these possible nucleation centres. Additionally, the amplitude of the peaks matching the crystallinity degree is larger for the thicker films, confirming that ordering in polycrystalline structures is more likely induced by a longer deposition duration at 60°C on the heated plate.

The optical properties of interest in glazing are significantly depending on the morphology that influences multiple scattering (thus, the optical reflectance) and by the thickness that has main consequences on the optical transmittance.

Table 2. Roughness, maximum on the pore size distribution curve (Φ_p), thickness (H), average TiO₂ crystallite sizes and crystallinity degree (χ) of SiO₂/TiO₂ multi-layered thin films.

Samples' code	Roughness (nm)	Φ_p (nm)	H_{exp} (nm)	H_{theory} (nm)	Crystallite size (Å)	χ (%)
Glass substrate	0.98	—	1.2×10^6	—	—	—
SiO ₂ _3 (1)	77.3	480	94.3	—	—	—
TiO ₂ _3 (1)	63.4	260	45.3	—	82.4	17.6
TiO ₂ _350AuNP_3 (1)	59.7	273.3	52.7	—	80.9	18.6
TiO ₂ _1500AuNP_3 (1)	84.1	720.1	53.1	—	81.1	18.7
SiO ₂ _TiO ₂ _3_3 (3)	94.5	500	172.9	233.9	85.4	18.8
SiO ₂ _TiO ₂ _350AuNP_3 (3)	95.2	300	174.1	241.3	81.9	20.2
SiO ₂ _TiO ₂ _1500AuNP_3 (3)	98.6	200	176.2	241.7	82.5	20.5
SiO ₂ _TiO ₂ _3_5 (5)	86.3	350	327	373.5	85.9	19.6

The SiO₂ monolayer has a less dense structure compared to the thicker TiO₂, but the addition of large amounts of gold nanoparticles (sample TiO₂_1500 AuNP_3) leads to a smooth surface morphology with very large open pores, confirming the nucleation role of the metal nanoparticles as the data in table 2 is outlined.

In multi-layered thin films, the effect of the initial silica layer supports the development of rough surfaces. However, the longer duration for cold spraying at 60°C required by the sample containing five layers (SiO₂_TiO₂_3_5) supports reorganization and/or pores filling, ending up in smooth surfaces with lower mezzo-pores. To evidence this effect, the theoretical thickness of the multilayers (H_{theory}) was estimated by adding the corresponding thicknesses of the monolayers; the values in table 2 show that the five-layered film is actually thinner than theoretically expected, thus, reorganization runs with densification. Additionally, the gold nanoparticles support densification as a result of enhanced nucleation and reorganization.

Not only the surface morphology, but also the powder-type aggregates sticking to the film surface can influence the optical properties. Therefore, surface morphology of the SiO₂-TiO₂ thin films was further analysed by low vacuum SEM without metallic coverage.

The monolayered films have no large aggregates, but the 3- and 5-layered structures have a surface covered with micro-metric sized aggregates, as a possible result of the deposition on already rough substrates and longer deposition duration (figures 2 and 3).

3.2 Optical properties

The prerequisites for the optical properties of the SiO₂-TiO₂ thin films deposited on solar collector glazings are: high transmittance ($T > 75\%$) and low absorbance ($A < 10\%$) in the UV-Vis-NIR spectral range, low UV-Vis reflectance ($R < 15\%$) and controlled refractive index. Thus, the optical properties of the thin films were investigated in the 250–2500 nm range, and the transmittance and reflectance spectra are presented in figures 4 and 5.

Except the sample with the highest roughness (SiO₂_TiO₂_3_3), all the other films supported increasing the transmittance (as compared to the microscopic glass substrate), confirming the role of silica, with low refractive index. All the films have high transmittance ($> 85\%$) over the entire domain, but almost constant and very large values (above 90%) correspond to the monolayers of titania with gold nanoparticles; the same films have the lowest reflectance values (10%), confirming the role of smooth morphology in very good optical properties.

The layer thickness was calculated using equation (2):

$$d = \frac{\lambda_1 \cdot \lambda_2}{2(\lambda_2 - \lambda_1)(n_i^2 - \sin^2 \alpha)}, \quad (2)$$

where λ is the wavelength corresponding to (λ_1) minimum reflectance and (λ_2) maximum reflectance; n_i the refraction index; and α the incidence angle (6°).

Smooth but thicker films (SiO₂_TiO₂_1500AuNP_3 and SiO₂_TiO₂_3_5) show transmittance decrease and higher reflectance (up to 12%), along with modulation in Vis and NIR, thus, there is an optimum between roughness and thickness that must be reached. This modulation can be the result of combining two materials with different refractive indexes: SiO₂ ($n = 1.45$) and TiO₂ ($n = 2.53$), and with different thicknesses, allowing to obtain shades of colours at different incident radiation angles; this represents an asset considering the aesthetic prerequisites as previously reported [23].

The solar-thermal devices convert the UV-Vis part of the solar spectrum into heat and transport the IR part through convection. As the Vis spectral range covers the largest energy share in the solar radiation, it is important to allow as much as possible of it to pass through the glazing and reach the absorber plate. Therefore, for analysing the optical performances and their stability in the thin silica and/or titania films, the corresponding transmittance and reflectance values at 500 and 700 nm were compared, and the data are included in table 3. The values in table 3 recommend the monolayers of

Figure 2. AFM images of the samples: (a) SiO₂_3; (b) TiO₂_3; (c) TiO₂_350AuNP_3; (d) TiO₂_1500AuNP_3; (e) SiO₂_TiO₂_3_3; (f) SiO₂_TiO₂_3_5; (g) SiO₂_TiO₂_350AuNP_3 and (h) SiO₂_TiO₂_1500AuNP_3.

titania with gold nanoparticles in having the best combination of optical properties, better as the initial glass substrate.

3.3 Contact angle measurements

Self-cleaning and photocatalytic properties are supported by good wettability, therefore, contact angle measurements were performed to investigate the influence of morphology and crystallinity on the surface energy. The contact angle decrease in time (figure 6) gives evidence on the surface morphology and/or chemistry. As the data in table 4 show that the water contact angles were low ($<15^\circ$), and complete water wetting occurred in <5 s, proving that the surface has high polar/ionic degree and a fractured morphology. To differentiate between the layers wettability, the contact angles corresponding to other two viscous liquids (glycerol GL, and polyethylene glycol PEG400) were registered and the

results well mirror the surface roughness, with large macro-heterogeneity for the 5-layered film (SiO₂_TiO₂_3_5) and two (or more) distinct groups of macropores for SiO₂_3 (thus, a sharp decrease in the contact angle after filling the larger pores). As both glycerol and PEG400 have moderate polarity (as compared to water), one may observe that the contact angles at the initial moment (table 4) show good solvophilicity. The timely evolution of the contact angle values also outlines the influence of the surface roughness, registered through sudden changes in the contact angle values in the first 25...30 s, followed by a stabilization. This is a typical evolution for the large open surface pores, inducing rather large roughness values. However, there are differences in the contact angles of the two organic liquids that result from the differences among their polarity (dielectric constants are quite different: 42.5 for glycerol and 12.4 for PEG400), promoting weaker solid-liquid interactions with PEG400,

Figure 3. SEM images of the samples: (a) SiO_2 _3; (b) TiO_2 _3; (c) TiO_2 _350AuNP_3; (d) TiO_2 _1500AuNP_3; (e) SiO_2 _TiO₂_3_3; (f) SiO_2 _TiO₂_3_5; (g) SiO_2 _TiO₂_350AuNP_3 and (h) SiO_2 _TiO₂_1500AuNP_3.

Figure 4. Transmittance spectra for SiO_2 / TiO_2 multi-layered thin films.

Figure 5. Reflectance spectra of the SiO_2 / TiO_2 multi-layered thin films.

Table 3. Transmittance (*T*) and reflectance (*R*) of SiO₂/TiO₂ multi-layered thin films at $\lambda = 500$ and 700 nm.

Samples' code	<i>T</i> ₅₀₀	<i>T</i> ₇₀₀	<i>R</i> ₅₀₀	<i>R</i> ₇₀₀
Glass substrate	91.42	89.45	10.52	10.29
SiO ₂ _3	90.85	90.36	10.39	10.17
TiO ₂ _3	91.05	90.58	10.55	10.30
TiO ₂ _350AuNP_3	91.15	91.76	10.19	9.81
TiO ₂ _1500AuNP_3	90.95	91.65	10.34	9.72
SiO ₂ _TiO ₂ _3_3	90.41	90.21	10.46	10.11
SiO ₂ _TiO ₂ _3_5	90.73	90.56	10.81	9.88
SiO ₂ _TiO ₂ _350AuNP_3	90.71	90.52	10.72	9.97
SiO ₂ _TiO ₂ _1500AuNP_3	90.72	90.50	10.69	10.04

thus, more steady kinetic curves in the contact angle evolution.

A good water wettability is prerequisite for interface-dependent application such as photocatalytic degradation of organic components in various environmental conditions. Using the Fowkes equation, equation (3) [24], the surface energy and its polar and dispersive components were calculated for each sample and the results are included in table 4:

$$\sigma_{LV} (1 + \cos \theta) = 2 \left[(\sigma_{LV}^p \sigma_{SV}^p)^{1/2} + (\sigma_{LV}^d \sigma_{SV}^d)^{1/2} \right], \quad (3)$$

where σ_{LV}^p , σ_{LV}^d , σ_{SV}^p and σ_{SV}^d are polar and dispersive components of the liquids and thin films surface energies, respectively. In this case, the initial angle between liquid and film surface was measured. Water was used as polar liquid ($\sigma^p = 52.20 \text{ mN m}^{-1}$) and glycerol was used as less polar liquid ($\sigma^p = 37.00 \text{ mN m}^{-1}$).

The surface energy is higher for rough surfaces (as for SiO₂_3, SiO₂_TiO₂_3_3 and SiO₂_TiO₂_350AuNP_3 samples) as the corners and edges are energy concentrators. However, the highest surface energy corresponds to the thickest sample (SiO₂_TiO₂_1500AuNP_3). This is outlined also by a faster decrease in the contact angle values in the first 30 s (using glycerol as wetting liquid) when the larger pores are filled in fast.

The correlation between morphology and surface energy indicates that high concentration of golden nanoparticles embedded in SiO₂-TiO₂ composite increases the surface roughness inducing higher surface energy values (from 104.3 mN m⁻¹ for SnO₂-TiO₂_3_3 to 401.1 mN m⁻¹ for SiO₂-TiO₂_1500AuNP_3).

Important to notice is also the larger share of the polar component for the TiO₂ monolayers (as a result of the higher ionic degree of titania as compared to silica) supporting the assumption of more active sites for further adsorption and photocatalysis. Although successively deposited, the thin titania and silica layers can interpenetrate resulting in a 3D composite thin film, exhibiting a larger share of TiO₂ at the surface. To test this assumption, surface composition was

Figure 6. Contact angle timely evolution using (a) glycerol and (b) PEG 400 liquids.

evaluated based on EDX analysis and the results are presented in table 5.

The data show a large amount of Si from the silica in the films (along with Na) and low amounts of Ti from TiO₂. Although low, this amount is larger in SiO₂-TiO₂_3_5 sample, explaining thus, the large share of the polar component in the surface energy. This exceedingly high surface silica also explains the apparent low crystallinity of the samples.

3.4 Photocatalysis results

The evaluation of photocatalytic activity followed two different pathways:

- (1) 6 h of samples immersion in MB solution under simulated solar irradiance (figure 7a);
- (2) 2 h of samples immersion in MB solution in dark followed by 6 h under UV-Vis irradiation (figure 7b).

Table 4. Contact angle measurements and surface energy of the samples.

Samples' code	θ_{water} (°)	θ_{GL} (°)	θ_{PEG400} (°)	Surface energy σ (mN m ⁻¹)	Dispersive component σ^d (mN m ⁻¹)	Polar component σ^p (mN m ⁻¹)
SiO ₂ _3	13.95	76.34	35.76	234.0	131.8	102.2
TiO ₂ _3	14.1	39.16	75.67	318.8	85.8	233.0
TiO ₂ _350AuNP_3	12.3	23.9	22.9	157.4	62.4	95.0
TiO ₂ _1500AuNP_3	13.5	32.1	23.25	173.3	76.2	97.1
SiO ₂ _TiO ₂ _3_3	10.1	62.80	26.61	104.3	45.6	58.7
SiO ₂ _TiO ₂ _350AuNP_3	11.3	31.56	18.87	225.6	41	184.6
SiO ₂ _TiO ₂ _1500AuNP_3	11.4	35.67	37.92	401.1	121.8	279.3
SiO ₂ _TiO ₂ _3_5	10.5	15.65	15.97	115.2	53.0	62.2

Table 5. Energy dispersive X-ray analysis of SiO₂/TiO₂ multi-layered thin films.

Samples' code	Atom%				
	Ti	Si	Na	Au	O
SiO ₂ _3	0	27.05	8.90	0	64.06
TiO ₂ _3	0.16	26.24	8.41	0	65.19
TiO ₂ _350AuNP_3	0.19	32.92	8.35	0.15	58.39
TiO ₂ _1500AuNP_3	0.12	29.66	9.05	0.30	60.87
SiO ₂ _TiO ₂ _3_3	0.05	26.89	9.69	0	63.32
SiO ₂ _TiO ₂ _350AuNP_3	0.08	26.62	9.56	0.08	63.66
SiO ₂ _TiO ₂ _1500AuNP_3	0.15	22.36	8.59	0.23	68.67
SiO ₂ _TiO ₂ _3_5	0.27	26.5	7.93	0	65.3

These comparative data give information about the influence of sample conditioning on the photocatalytic efficiency. The highest photocatalytic activity/efficiency was observed for the SiO₂-TiO₂_3_5 sample, also showing the highest amount of surface titania, while the lowest value was recorded for SiO₂_3 thin film with well-known high band gap [25]. In the most effective case, the photocatalytic activity reaches 40% when 2 h of dark immersion is used, compared with 22% when no initial absorption was employed. This effect is registered for each film, thus, a conditioning step involving adsorption, can be beneficial for effective self-cleaning glazings.

The samples (SiO₂-TiO₂_3_5 and SiO₂-TiO₂_3_3) with the highest hydrophilic surface also have high photocatalytic efficiency which is an advantage in glazing/fenestration self-cleaning. Except the TiO₂_350AuNP_3 film, all the other samples containing gold nanoparticles register an increase in the photocatalytic activity when an initial 2 h absorption in dark is used as conditioning step. As expected, good photocatalytic efficiencies were obtained for the thin films containing only TiO₂ with promising values for the smooth films containing gold nanoparticles.

Another important feature is the durability of the photocatalytic films, both in absorption and photocatalysis. The changes in the transmittance values (at 500 and 700 nm) of

the films immersed in MB solutions, after 0...6 h of photocatalysis or 0...2 h of adsorption were measured and the results are presented in figure 8.

Adsorption and photocatalysis lead to a transmittance increase, higher in dark (~1%) and lower during the 6 h of photocatalysis. Two significant aspects should be outlined related to the slope in the transmittance variation: it is almost constant for all the thin films and is equal with the corresponding value of glass (non-coated substrate). This allows to conclude that transmittance increase is not the result of a thin film wash-out effect, but may be related to the pollutant interaction with the glass part (back side) of each thin film.

4. Conclusions

Eight multi-layered thin films of SiO₂ and TiO₂ were obtained and characterized aiming at applications as glazing in flat-plate solar-thermal collectors with optimized optical and self-cleaning properties. The results indicate that the addition of gold nanoparticles in the SiO₂-TiO₂ multi-layered thin film structures leads to lower surface roughness, but have no significant impact on the photocatalytic efficiency.

Figure 7. Photocatalytic activity in MB solution: (a) without and (b) with 2 h of immersion in dark.

Good optical properties were obtained for all the thin films containing TiO₂ or SiO₂-TiO₂ combined layers, with transmittance values above 90% and reflectance of 10% or lower in the Vis spectral range. The best optical properties, better than the uncoated glass, correspond to the titania thin films obtained with addition of gold nanoparticles (TiO₂_350AuNP_3 and TiO₂_1500AuNP_3) that act as nucleation centres allowing more organized aggregation of the initial nanoparticles.

The best combination of optical properties and photocatalytic efficiency was recorded for the SiO₂-TiO₂_3_5 sample, as a result of an interpenetration of silica and titania layers in a 3D composite structure, with thickness of about 400 nm. The durability tests indicate that all samples are chemically stable after 6 h of photocatalytic activity. Additionally, the combined effect of high/super-hydrophilic surface and good photocatalytic properties recommends the

Figure 8. Transmittance changes in the thin films measured at (a) 500 and (b) 700 nm.

SiO₂-TiO₂_3_5 sample as a suitable candidate for self-cleaning, high-transmittance coatings in FPSTC or in fenestration applications.

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