



SILICA THIN FILMS OBTAINING BY SOL – GEL DIP COATING WITH CONTROLLED OPTICAL PROPERTIES¹

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ABSTRACT

Transparent oxide films are widely employed as antireflection or high reflection coatings, band-pass filters and narrow-band-filters in various optical and electronic devices. The performances of these devices are based on interference effects obtained by alternating layers of high and low refractive indices. Different deposition techniques have been employed for coating glasses with different thin films materials. The metal oxides optical coatings can be deposited on glass substrate by CVD and PVD processes. The heterogeneity between the deposit and the glass substrate is the principal cause of the lack of durability of these coatings. Mono or multilayers materials could be used as colored glazing, which is slightly opaque to the human eye but highly transparent to solar energy. The glazing colors are based on interference in the thin-film coating(s) on the reverse side of the glass. Our research group focuses on investigation of single SiO₂ and SiO₂-TiO₂ multilayers, obtained by dip-coating (DC) deposition technique using sol-gel precursors, as suitable glazing for colored solar-thermal collectors.

By optimizing the deposition parameters (number of deposition sequences, time between deposition sequences, immersion and extraction rate, temperature) and the precursor properties (concentration, additives, etc.) we are able to tailor the morphological and optical properties of silica coated glass. Consequently the transmittance has increased up to 93% in UV-VIS and IR regions and the reflectance is < 5% in VIS and IR regions.

The samples show various morphologies (mostly dense with grains around 30-40 nm) function of the precursor composition (presence of additives) and concentration.

KEYWORDS: SiO₂, coating, sol-gel, morphology, optical properties

1. Introduction

One of the most abundant renewable energy sources is solar energy and conversion systems are developed for producing power (photovoltaic systems) or heat (solar-thermal systems). Among these, the most efficient use of solar energy is in solar-thermal systems using solar thermal collectors [1]. Many of these systems are used in order to reduce

the conventional energy demand in public buildings, residential areas [2], and industrial consumers [3].

Nowadays the solar thermal collectors are systems designed to increase solar energy efficiency, quality, life expectancy and profitability.

To fulfill these requirements, but also for decreasing the related building materials costs as well as the necessary time for their installation, the implementation of low cost, high efficiency solar thermal collectors are required [4]. Additionally, for implementing such collectors in the built environment, architectural and aesthetical constraints must be fulfilled. A perfect architectural integration of common glazed or unglazed solar thermal collectors in a building is difficult to obtain.

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This would mean that the collector is part of the building's envelope or an architectural design element and can therefore not be recognized immediately as a solar collector [5]. Therefore, recent studies show more and more the tendency of coloring the solar thermal flat plate collectors that are usually recommended for buildings' implementation, as they are delivering the thermal agent at a convenient temperature of 80...110 °C. There are two main ways for coloring solar thermal collectors: by coloring the absorber plate or by coloring the glazing.

The performance criteria of the coating glazing in the solar thermal applications are connected to three factors: high transmittance in UV-VIS-NIR, low reflectance in UV-VIS and chemical stability in the operating conditions: humidity, dust and high exposure to climatic phenomena.

The thermal transmittance, solar and visible transmittance are the main parameters in studying the performance of advanced glazing systems. By adopting double and triple glasses or modern double skin facades, the ratio between transmission and reflection could be reduced [6].

On the other hand, glazing can be colored by tuning the optical properties of multi-layers with different refractive indexes. Such a combination is represented by the silica/titania multi-stacks. A method for obtaining SiO₂/TiO₂ thin films was proposed on the ion beam induced and plasma enhanced chemical deposition [7]. The authors concluded that the refractive index of the film is directly correlated with the titanium content inside the film. It was studied the possibility to integrate dielectric multilayer films of Al₂O₃/SiO₂ and TiO₂/SiO₂ as a colored glazed cover for thermal solar collectors [8]. These multilayer films have been obtained by alternative deposition of dielectric layers with high and low refractive indices.

The authors determined the optical properties of individual oxides of titanium, silicon and aluminum. They observed that the reflectivity and the solar transmission depended on the thickness and the number of alternative dielectric layers in the thickness sensitive thin layers. Cianhung Huang *et al.* prepared a neutral SiO₂/TiO₂ composite hydrosol by the coprecipitation-peptization method. They used titanium tetrachloride and silicon dioxide hydrosol as precursors.

The authors observed that the additive SiO₂ decreased the refractive index and suppressed the aggregation of TiO₂. The results showed that the lower refractive index of SiO₂/TiO₂ thin film could increase the transmittance of visible light [9].

Thus, optimized deposition should be found for each of the component layers. This paper focuses on the SiO₂ layers, where plenty of work is already reported.

Miyazaki and Goto proposed a method to obtain SiO_x film based by RF magnetron sputtering process. This method is very effective for surface modification and consists of ejecting the atoms from a target material and condensing the ejected atoms onto a substrate in a high vacuum environment [12]. In order to obtain the silica thin films, other different methods can be used: chemical vapor deposition (CVD), physical vapor deposition (PVD), reactive magnetron sputtering [13] or spray pyrolysis deposition [14].

Although performant, these reports rely on high-cost deposition methods, therefore alternative investigations should be needed. The sol-gel process represents a method to produce solid materials from small molecules and is especially used for the fabrication of the silicon and titanium oxides. This process involves the transformation of monomers into a colloidal solution (sol), which acts as a precursor for discrete particles or network polymers [10]. The method has the advantages of simplicity and low cost, it is applied at low processing temperature; it has as a result the homogeneous films on glass with high optical properties [15]. Research groups have used the sol-gel process to prepare silica/titanium hybrid films with refractive index varying from 1.44 to 2.20. This film is applied for the triple layer broadband AR coating. One mechanical performance of this film and the morphology of the obtained coating were investigated [11].

After preparing the gel, the deposition could be directly done by various methods, among which dipping represents a feasible alternative [16].

This paper reports the novel results obtained in optimizing the sol-gel SiO₂ preparation and the development of the optimized thin layers deposition by dipping, targeting optimized and performant optical properties, as a first step in obtaining colored glazing for novel flat-plate solar-thermal collectors for the built environment.

2. Experimental part

The silica hydrophilic coating sol was prepared by mixing the tetraethyl orthosilicate (TEOS, 99%), absolute ethanol (EtOH 99.5%), pure water, hydrochloric acid in the volume of (1:8:3:0.5). The mixture was then stirred at 60°C for 2h and aged for 7 days. Silica thin films were deposited on glass substrate (2.5×2 cm²) by dip – coating technique using speed of 5mm/min. The glass substrates were cleaned previously by ultrasonic equipment in alcohol and then dried using compressed air.

In this study, the parameters that were varied are: number of dipping sequences (6, respectively 10), the amount of gel (0.5; 1; 1.25; 1.5; 1.75; 2 g) dispersed in 50 mL ethanol : water (1:1 v/v) mixture.

For improving the layers homogeneity, the addition of a surfactant was tested: dodecyl-trimethylammonium bromide, DTAB. The tests were developed in parallel series, with and without DTAB addition and the optical properties were comparatively discussed.

The silica thin films obtained were introduced in an oven at 120 °C for 2 hours for drying and slightly sintering. The morphological properties of silica thin films were analyzed using Atomic Force Microscopy (AFM/STM, NT-MDT model NTEGRA Probe Nanolaboratory), in semicontact mode.

The optical properties and the thickness layer were determined by using UV–VIS–NIR spectroscopy (Perkin Elmer, Lambda 950 model, equipped with 150 mm integrating sphere).

Contact angle measurements were done using the sessile drop method (DataPhysics Instrument), and using water as wetting liquid.

3. Results and discussions

The optical properties are significantly influenced by: the layers thickness and by the surface roughness (inducing multiple reflections but also scattering). The thickness of the silica thin films increases with the number of immersions but not linearly probably because the deposited layers are going through a re-organizing process in sequential depositions, Fig. 1.

For the silica thin films with DTAB an increase in the layer thickness is observed, due to the ability of the additive to improve the wetting surface and facilitating the adhesion of SiO₂ to the substrate. Thus, when using DTAB, thin films are obtained with higher thickness even if using the minimum amount of gel (0.5 g). Additionally, the mild thermal treatment allows for re-organization in the thin films that are more obvious in films obtained using larger amounts of gel.

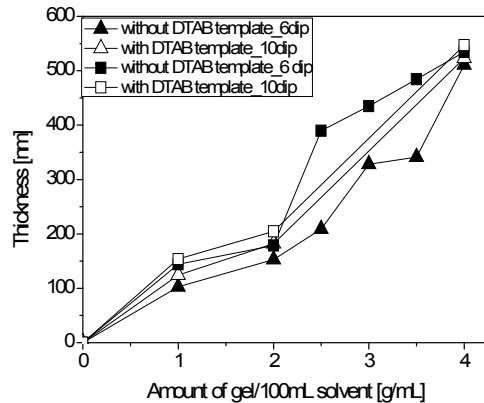


Fig. 1. The thickness layers of the silica thin films

It is interesting to notice that, regardless the surfactant addition and the number of immersions, the films obtained with large amount of gel (4 g gel/100 mL solvent) have an almost identical thickness, perhaps as result of reaching a stable surface aspect.

By varying the number of immersions from 6 to 10, for different gel compositions, the morphology of the thin films changed, too, Fig. 2.

The SiO₂ sample with 1 g gel/100 mL has the highest roughness value, and corresponds to a rather inhomogeneous thin film. Increasing the amount of gel leads to a slight roughness decrease up to a certain amount (2.5 g/100 mL), above which the roughness increases as result of the development of thicker, less ordered films.

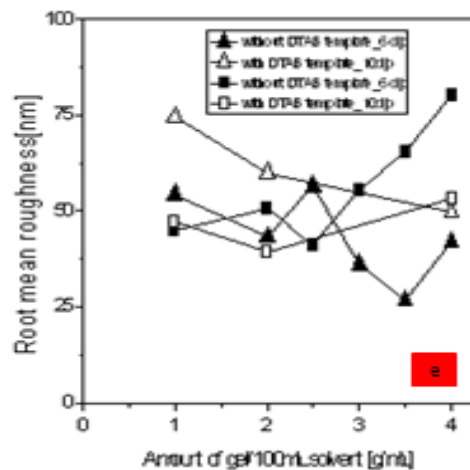
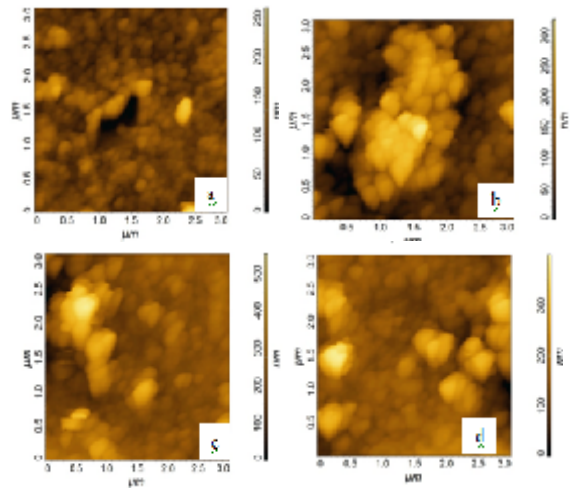


Fig. 2. AFM images for the sample: (a) 4.0 g 6dip; (b) 2.0 g DTAB 6dip; c) 2.0 g 10dip; (d) 4.0 g DTAB 10dip and the variation of the root mean square roughness (RMS) with the amount of gel in 100 mL solvent (e)

The surfactant addition has also as effect an increase in the surface roughness for the samples

obtained with higher amounts of gel, as a possible result of an “ordering” effect among the silica nanoparticles, that leads to less dense structures (with higher thickness) and with large open pores. Still, the AFM images also show the “macro-smoothing” effect of the surfactant that prevents surface agglomerations, leading to more homogeneous surfaces. The wettability of the thin films is important, as in the working environment, thin water films can condense on the grazing and lead to the distortion of the optical properties or to erosion. The values of the contact angles of water on the thin films were measured immediately after depositing the liquid drop and are presented in Table 1. The water contact angles are low, corresponding to hydrophilic (for several samples to super-hydrophilic) surfaces.

Table 1. Water contact angle variation on the silica thin films

Samples without DTAB addition	Contact angle [deg.]	Samples with DTAB	Contact angle [deg.]
SiO ₂ 0.5g_6dip	22	SiO ₂ 0.5g_DTAB_6dip	18
SiO ₂ 1.0g_6dip	15	SiO ₂ 1.0g_DTAB_6dip	17
SiO ₂ 1.25g_6 dip	25	SiO ₂ 1.25g DTAB_6dip	25
SiO ₂ 1.5g_6dip	36	SiO ₂ 1.5g DTAB_6dip	13
SiO ₂ 1.75g_6dip	11	SiO ₂ 1.75g DTAB_6 dip	16
SiO ₂ 2g_6 dip	17	SiO ₂ 2g DTAB_6 dip	9
SiO ₂ 0.5g_10dip	14	SiO ₂ 0.5g_DTAB_10 dip	17
SiO ₂ 1.0g_10 dip	27	SiO ₂ 1.0g_DTAB_10dip	29
SiO ₂ 2g_10 dip	14	SiO ₂ 2g DTAB_10 dip	12

The results are following an almost identical trend with the roughness, proving that the morphology is mostly responsive to this behavior and not the chemical composition. As expected, surfactant addition has as result a slight lowering in the contact angle, proving its preferential adsorption on the grains surface. The most important optical properties for glazing are: in UV–VIS–NIR range ($T > 70\%$), low reflectance in UV–VIS range ($R < 15\%$), low absorbance in UV–VIS–NIR range ($A < 10\%$), and

controlled refractive index. The silica thin films with and without DTAB addition were investigated by spectral analyses within the 250–2000 nm range.

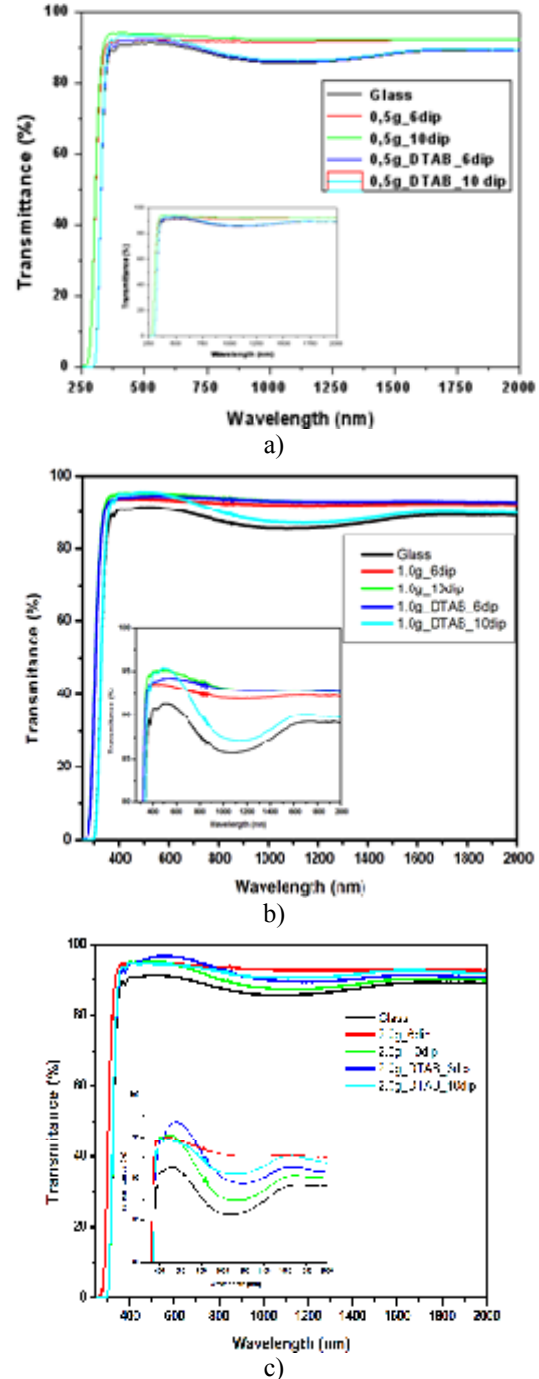


Fig. 3. Transmittance spectra for silica thin films by dip-coating obtained using: (a): 0.5 g; (b): 1 g; and (c) 2 g gel in 50 mL mixed solvent

In Fig. 3 there are presented the transmittance spectra for SiO₂ thin films deposited on glass substrate with and without addition of the DTAB

template. These thin films have increased transmittance in the UV range and slight modulation in the VIS and NIR regions, as compared to glass substrate (which has $T = 91\%$). In all situations, the transmittance values are above 80%, making thin films suitable in developing competitive glazing.

The transmittance spectra register the modifications mainly due to the different thickness of the films and its correlation with the refractive index, [10]. High values of the transmittance spectra increase to shorter wavelengths, which is a positive result for solar thermal flat plate collectors that are using high energy solar radiation to convert it into heat. The highest transmittance value (94...95%) appears at 500...600 nm, in the VIS spectral region, while the lowest values correspond to NIR (86...89%). The maximum transmittance values on the three spectral regions of interest (UV, VIS, NIR) are presented in Fig. 4, correlated with the concentration of gel in the deposition suspension. The data show a general trend of decreasing the maximum transmittance values from UV towards NIR for all the films, with values above 90% for the most important spectral regions: UV and VIS.

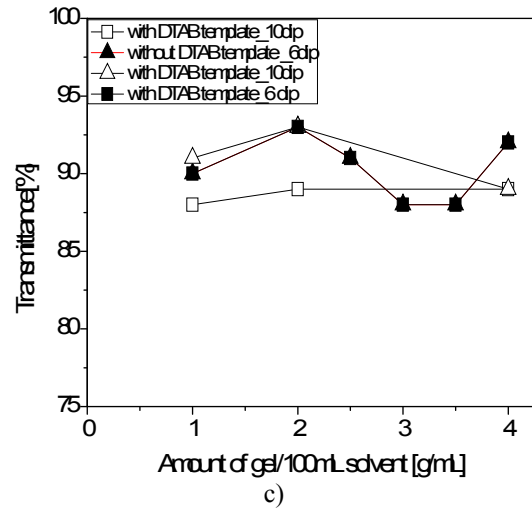
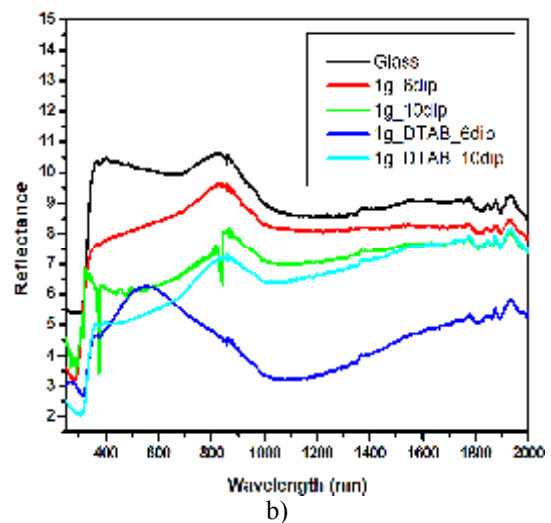
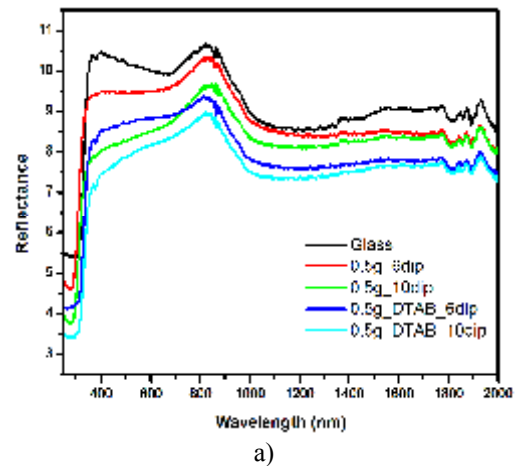
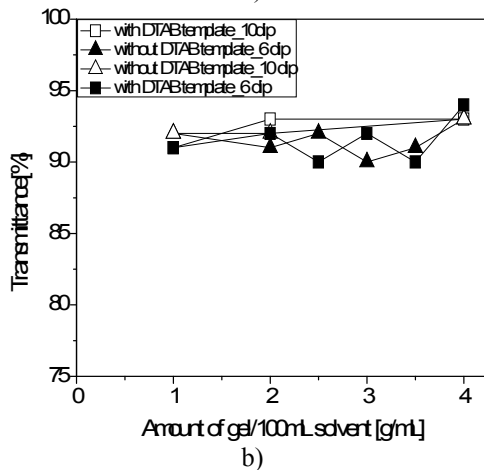
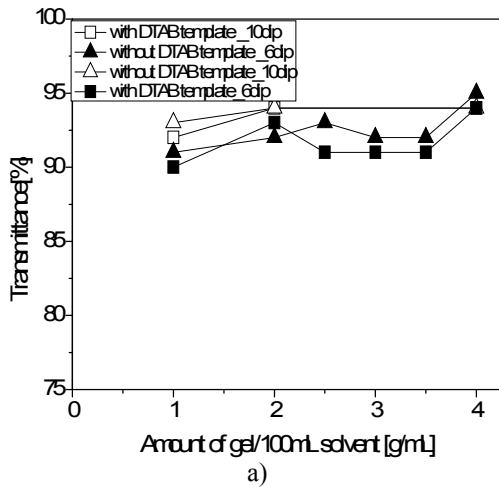


Fig. 4. Maximum transmittance of the silica thin films, within the spectral range: (a) UV, $\lambda = 250...300$ nm; (b) VIS, $\lambda = 300...800$ nm; (c) NIR, $\lambda = 800...2000$ nm



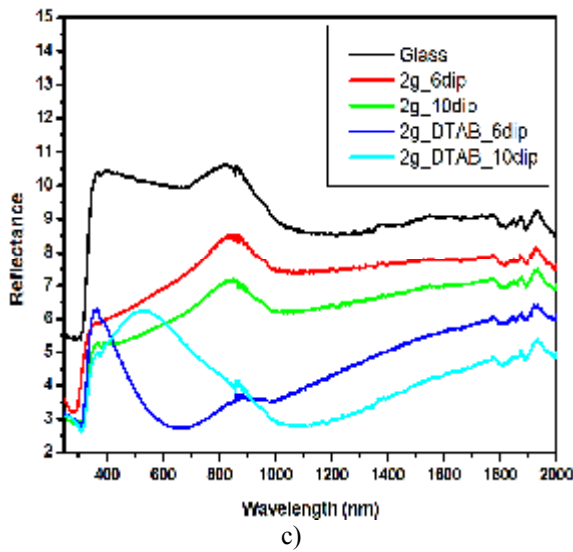


Fig. 5. Reflectance spectra of the silica thin films obtained using: (a) 0.5 g; (b) 1 g; and (c) 2 g gel in 50 mL mixed solvent

For the sample obtained by six immersions, the DTAB addition leads to the transmittance values, mainly as consequence of the ordering effect that decreases scattering. The best transmittance values are obtained for the films containing 1g gel/50mL solvent (2g/100mL). For glazings, reflections and scattering need to be minimized as being one main cause of losses.

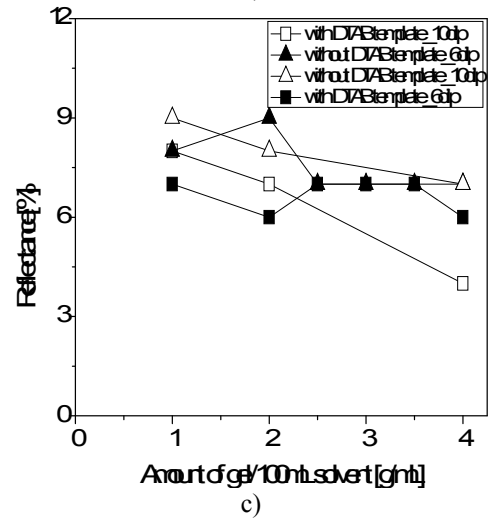
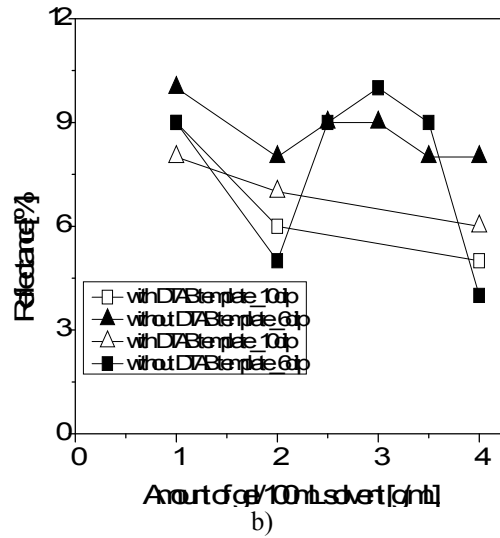
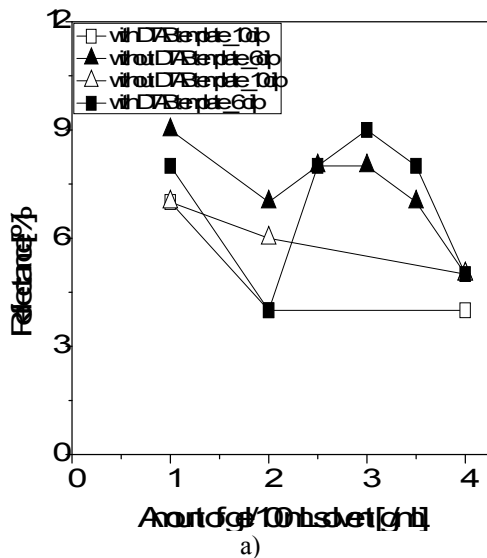


Fig. 6. Maximum reflectance of the silica thin films, within the spectral range: (a) UV, $\lambda = 250...300 \text{ nm}$; (b) VIS, $\lambda = 300...800 \text{ nm}$; (c) NIR, $\lambda = 800...2000 \text{ nm}$



The reflectance (R%) values are presented in Fig. 5. The results show that the films obtained using DTAB always have the lowest R% values and this could be corroborated with the lower roughness values, this lower multiple reflections.

This effect is more evident for the homogeneous presented in Fig. 5b and c. As in the case of the transmittance analyses, the best samples are those obtained using 2g gel/100mL solvent, and among these, the sample obtained with DTAB performs best.



4. Conclusions

Thin films of silica used in developing coloured glazing were obtained by using sol-gel synthesized nanoparticles and by the direct gel deposition, at various concentrations, by dipping. The results show that the number of dipping sequences and the gel concentration need to be inter-correlated, for obtaining smooth, low roughness films, with hydrophilic properties. The addition of a surfactant DTAB can improve tuning the optical properties and support optimization.

The silica thin film with good optical properties such as high transmission, low reflectance and low roughness obtained by sol-gel dip – coating methods is SiO₂ 1g DTAB_6 dipping dispersed in 50 mL ethanol: water (1:1v/v) mixture.

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