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Stable Multilayer TiO_2–SiO_2 Coatings for Antireflection Applications[1]

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Abstract—In this paper, multilayer TiO_2–SiO_2 containing polydimethylsiloxane (PDMS) coatings were produced by using sol-gel method. To further investigate, the effect of triton as a non-ionic surfactant on PDMS modified single and multilayer silica and titania coatings was studied. The results showed stability of optical triton containing coatings disappears with time due to this material improve the wetting properties of PDMS sols and helps to instability by water absorption. But without triton, antireflective multilayer coatings with high transmittance 98% and excellent durability were obtained by using PDMS as additive material. This coating can be used as well as in solar applications.

Keywords: sol-gel, thin film, antireflective, titania-silica, PDMS, triton

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INTRODUCTION

It is well known that the use of glass with antireflective (AR) surface instead of a normal glass as cover for solar thermal collectors, allows increasing the efficiency of the system [1]. Since the optical coatings are used outdoors, in addition to antireflective properties, abrasion resistance and moisture resistance as a result of climate change must be having. In order to cover the lower refractive index must be air-filled porosity. If the porosities are filled with other objects, index of refraction and reflection increases. So, stability of antireflection coatings for the solar collector is very important [2]. Usually, porous hydrophilic silica sol-gel coatings are used. As a result, they tend to absorb water from the surrounding environment. Water absorption leads to an increase in the refractive index of the coating and antireflective property is reduced. The introduction of hydrophobic groups in antireflective coatings is a good way to reduce water absorption. Polydimethylsiloxane (PDMS) molecules with hydroxyl and methyl groups are part of the material are hydrophobic. PDMS surface hydroxyl groups and hydroxyl groups can be dehydrated silica particles, thereby creating a covalent bond between the silica particles. Polymer binder leads to covalent bonding between the particles and thus a strong bond is formed. Also, toughness and flexibility PDMS gel network by reducing the pressure in the capillaries, thus increasing the thickness of coatings can produce more without cracking [3]. Triton is also commonly used as a non-ionic surfactant and effective porosity of the final film is used. Organic bonds are removed because of the heat. This event will lead to a lower refractive index. The antireflection film is higher when more than triton is used [4]. In this paper, the effect of PDMS and triton addition on multilayer antireflective titania and silica coatings were investigated.

EXPERIMENTAL

Silica and titania solutions containing hydrophobic PDMS were prepared. The chemicals used in making solutions were tetraethyl orthosilicate (TEOS, Merck Chemicals, purity >98%); tetrabutyl orthotitanate (TBOT, Merck Chemicals, purity 98%); absolute ethanol (EtOH, Merck Chemicals, absolute grade); Distilled water (H_2O); Nitric acid (HNO_3, Merck Chemicals, purity 65%); ethyl acetoacetate (EAA, Sigma-Aldrich Chemicals, purity 99%); triton X-100 (TX-100, Sigma-Aldrich Chemicals, purity 99%), polydimethylsiloxane (PDMS, Sigma-Aldrich Chemicals, purity 99%). Silica and titania sols were prepared by mixing TEOS : H_2O : *Et*OH : HNO_3 at 0.5 : 3.5 : 0.35 : 0.005 molar ratios and TBT : *Et*OH : H_2O : HNO_3 = 1 : 114 : 2 : 0.32 respectively. In all sols, the weight ratio of PDMS to SiO_2 and TiO_2 was 30%. To evaluate the

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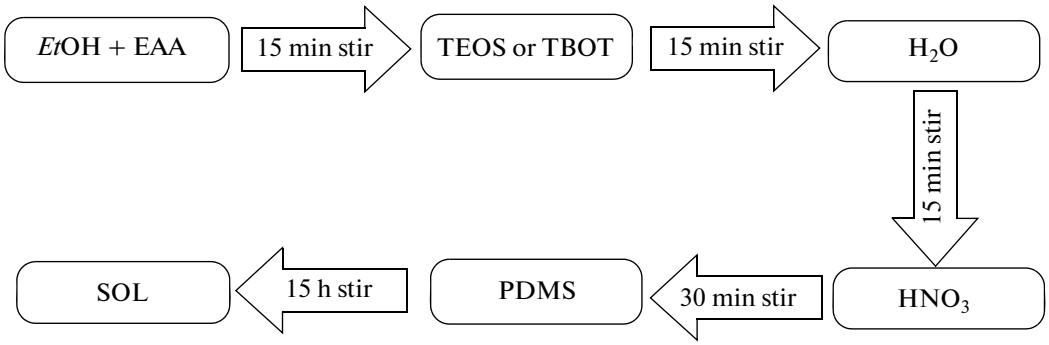

Fig. 1. Preparation of SiO_2 and TiO_2 sols.

effect of triton, another silica sol, including triton additive was prepared. Triton® X-100 at 40 g/L concentrations as a pore generator was added to silica sol. The preparation of sols can be seen in Fig. 1. Samples were prepared according to Table 1. Silica and titania layers are named *s* and *t* and with and without triton coatings are named *n* and *p* respectively. All the films were fabricated by dip-coating, the sols on microscope slid glass substrates, using a withdrawal speed of 25 mm/min. For single silica and titania coating, in one layer immersion time is 30 s and for double layer 30 s were examined. For multilayer coating each layer 30 s is being considered. Heat treatment at temperatures of 80 and 160°C for 3 h was performed. For evaluation of coatings, the optical behavior of coatings was examined by UV-VIS (Bruker Tensor 27). The wavelength range of 300–900 nm was measured by this instrument. The ellipsometry (SENTECH SE850 UV) was used to observe refractive index and thickness of single layer coatings. To study the functional groups exist on the surface, the infrared spectroscopy FT-IR (Jasco v-550) was used. Absorption spectroscopy was performed in the range of 400–2200 cm^{-1}. In order to study the morphology of the multilayer coatings, scanning electron microscope FE-SEM was used.

Table 1. Single and multilayer coating structures

p Sample	*n* Sample
sp-30	*sn*-30
sp-3030	*sn*-3030
ts-p	*ts-n*
sts-p	*sts-n*
tsts-p	*tsts-n*
tststs-p	*tststs-n*
tp-30	*tp*-30

RESULTS AND DISCUSSION

Coating infrared spectroscopy curves were shown in Fig. 2. The bands in 450, 800 and 1080 cm^{-1} related to the stretching vibration, bending and asymmetric bridges respectively [5–7]. Titania bonds between 500 to 900 cm^{-1} [8–9] and Si–O–Ti bonds occur at 920–960 cm^{-1} [10–12]. In the single titania curves, titania phases below 900 cm^{-1} can be seen. The intensity of peaks in the chart of double layer titania, is higher. A significant peak in the graph once titania layer occurred at 1360 cm^{-1} and 1840 cm^{-1} that were related to C–O–C bond and stretching vibration O=C [13]. Curves *Sp*-30, *ts-p*, *tsts-p* and *tststs-p* show similar behavior. Only double immersion spectroscopy silica coating with different behavior is shown. It seems chaotic surface than other surfaces. In almost all *p* curves, frequency ranges from 3000–1350 cm^{-1}, links to submix of bonds remains volatile organic compounds, water molecules and the SiO_2 network. The peaks at 1530, 1670, 1880 and 2100 cm^{-1} relate to these bands. The functional groups at 1530 and 1670 cm^{-1} relating to carbon bonds, the bonds sub-silica peak at 1880 and 2300 cm^{-1} for the absorption of CO_2 during the samples are prepared [14]. The bending vibration bands of water due to physical water environment absorption at 1640 cm^{-1} wasn't seen in the graphs. So PDMS as a hydrophobic material played its role well. Peak at 913 cm^{-1} in the figures with moderate intensity is related to the Si–CH_3 symmetric deformation of the PDMS. This peak indicates that the methyl groups are present in the modified coating with PDMS [8]. Peak intensity at 960 cm^{-1} for weak Si–OH and Si–CH_3 is high. This show, being dehydrated and PDMS will have happened between silica particles [15]. Strong peak at 800 cm^{-1} relating to the bending vibrations are bonded silica. In Sp-3030 curve the intensity of the peak at 530 cm^{-1} for the double bond C=CH_2 is small but highly peak around 1100 cm^{-1}, which is related to silica, was observed. The mean intensity peak at

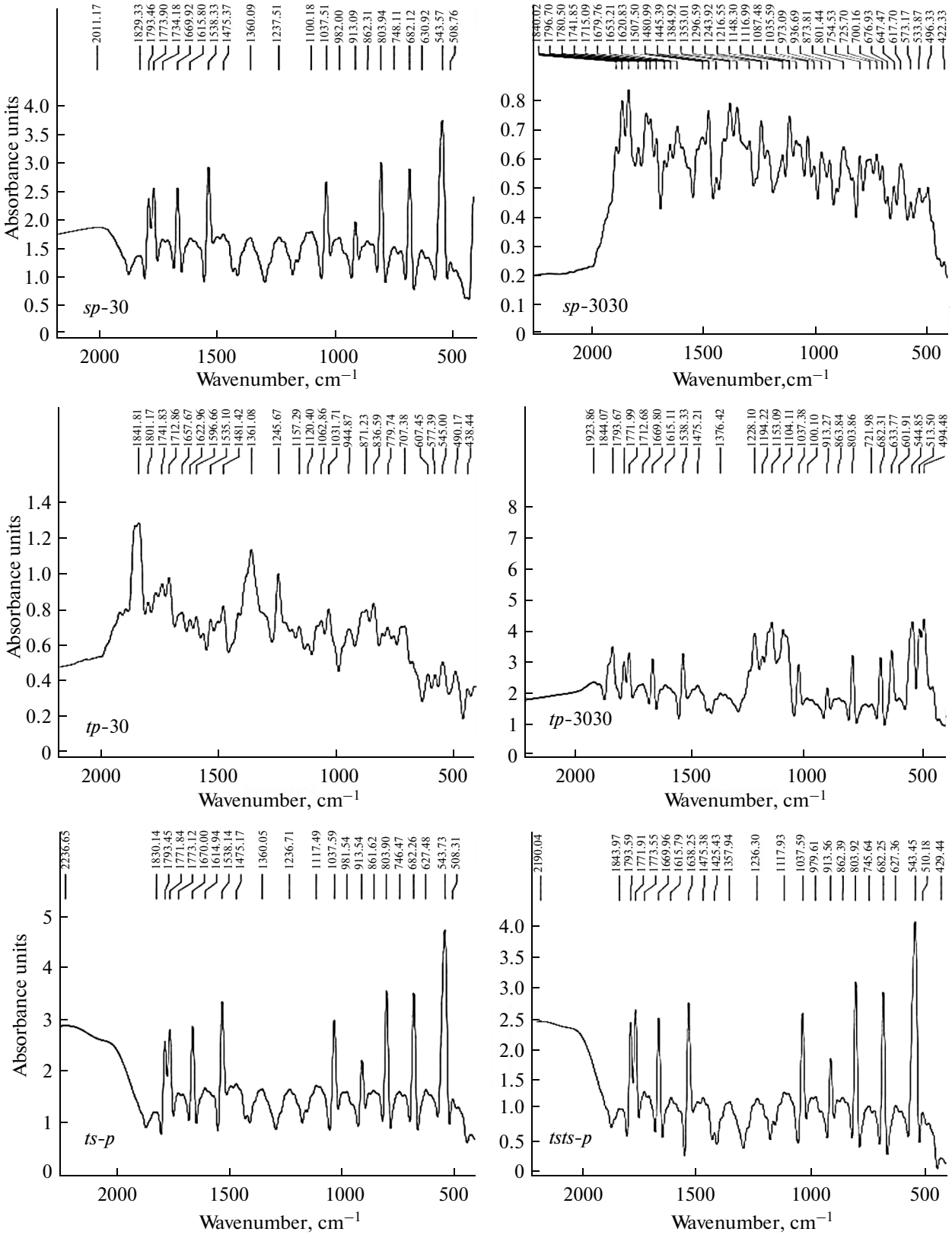

Fig. 2. FT-IR spectra of single and multilayer coatings.

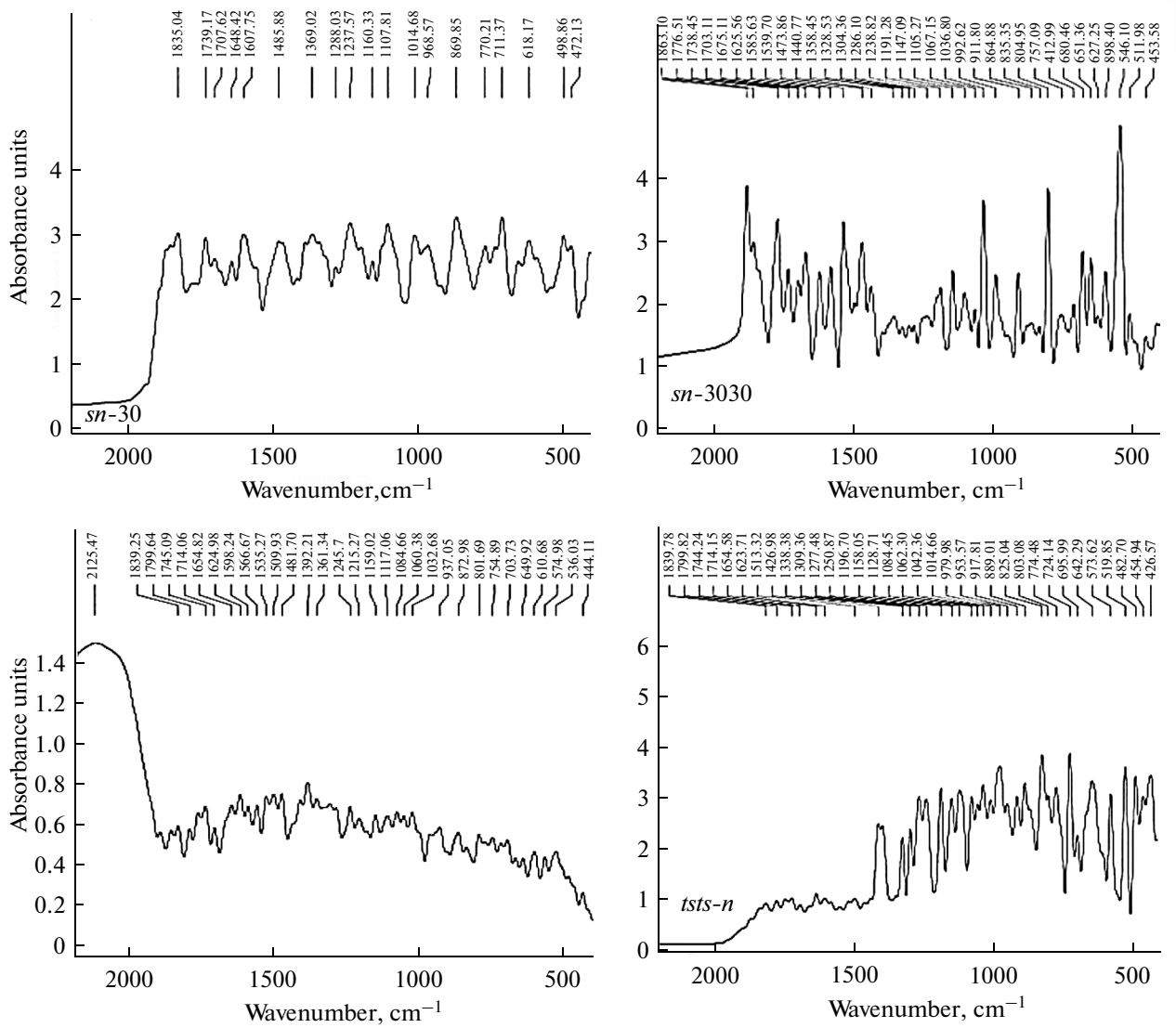

Fig. 2. (Contd).

1650 cm^{-1}, which show the absorbed water from the environment in all *n* curves, was observed. Triton X-100 is a non-ionic surfactant that has a hydrophilic polyethylene oxide chain led to this event. Also, researchers found that triton has led to improved wetting properties of the PDMS solution [16]. Titania anatase peaks weren't observed in all figures can be said with regard to the heat treatment temperature, amorphous silica and titania phases were formed. It should also be said about the same peaks of *p*, and had a clearer and less confusion.

Transmission spectroscopy results are shown in Fig. 3. The maximum transmittance of coatings is observed in Table 2. As you can see from the coating, four layer *tsts-p* and two layer *ts-p* coatings with 98%, 95.25% show favorable results compared to uncoated glass. Transmission of single layer silica—PDMS coating without triton with 30 s immersion is 94% and with two immersions is about 92.5%. One reason for the reduction of transmittance is increasing the thickness of the coating with two immersions. The behavior of bilayer coatings with two maxima at 580 and 350 nm has a W-shape behavior. In two and four layer coatings, the amount of light in the range 450–500 nm has further improved to 98%. Although, more coverage up to a maximum of six layers, transmittance discounted 75% or more. One reason for this is to create a thick coating. The *sts-p* coating transmission has fallen sharply. In containing triton samples with an extension as can be seen, with increasing layers, transmission gradually increased. However, in this case compared to uncoated glass is not a desirable result. Some *p* group coatings showed the best transmittance. Table 3 shows

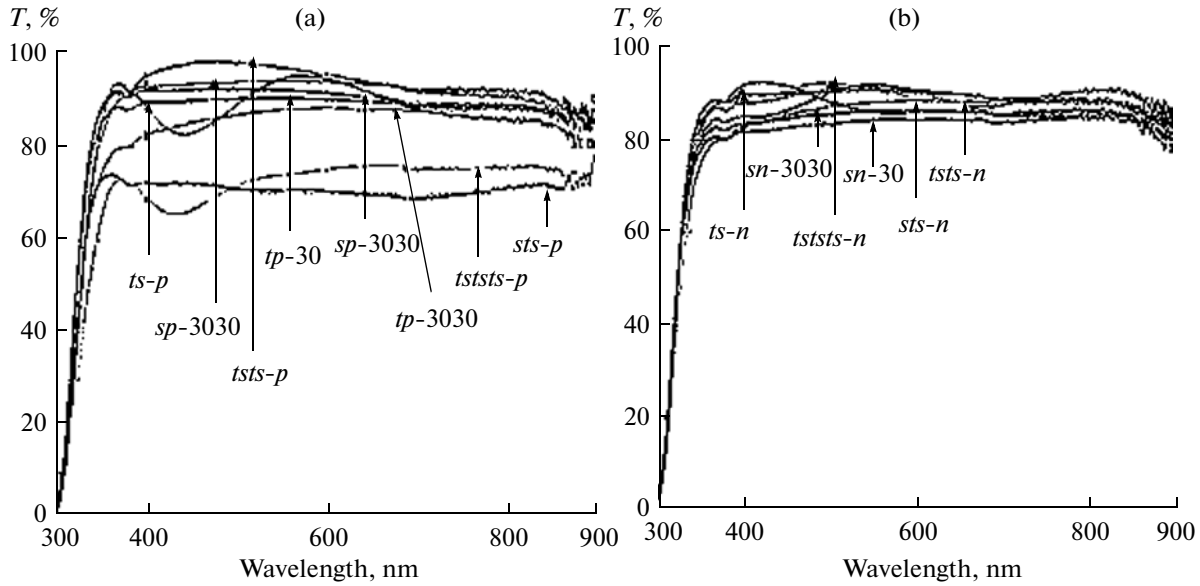

Fig. 3. UV-VIS transmittance spectra from 300 to 900 nm of the samples: *p* (a), *n* (b).

the effect of PDMS and triton material on refractive index and thickness of AR coatings. The refractive index decreases with the addition of PDMS. Results from the elliposometry show that the thicknesses of normal and PDMS modified silica AR coatings are, respectively 153 and 914 nm while the refractive indices are 1.48 and 1.44, respective. The PDMS modified silica sol contains larger particle size, which leads to a higher porosity and lower refractive index. The same event occurs for PDMS modified titania coating. But, in triton-PDMS modified coating, the refractive index is increased compared normal SiO_2 coating. Increase in refractive index due to the high refractive index of triton (1.49) can be expected. On the other hand, Bautista and Morales reported that silica films prepared with triton additive, the pore size is very small and

Table 2. Maximum transmission of coatings

Sample	Maximum transmission	λ_{max}, nm
tp-30	88	600–800
tp-3030	85	800
sp-30	94	500–600
sp-3030	92.5	400–550
ts-p	93.5, 95.25	350, 580
sts-p	74	350
tsts-p	98	450–500
tststs-p	75	600–800
sn-30	85	800
sn-3030	87	600–700
ts-n	92.5, 91	420, 800
sts-n	91.25	500–600
tsts-n	92	550
tststs-n	92.5	500

Table 3. Refractive index and thickness of single layer coatings

Sample	*n* (refractive index) at 550 nm	Thickness, nm
tp-30	1.60	254
sp-30	1.44	914
sn-30	1.66	1256
s-pure	1.48	153
t-pure	1.94	56

polymeric method produces stronger linkages [4]. The transmittance of the triton coating due to fine pores and high refractive index decreased. It is obvious that the presence of a non-ionic surfactant in sol solution causes the thicker coating. The maximum situation moved from a short wavelength to a longer wavelength

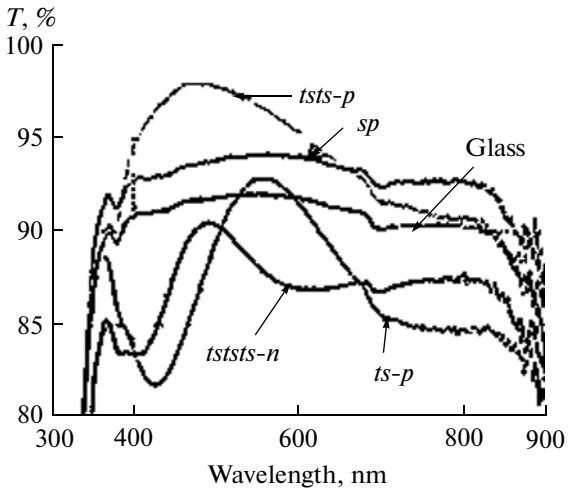

Fig. 4. UV-VIS transmittance spectra from 300 to 900 nm of the uncoated glass and coatings after 5 months.

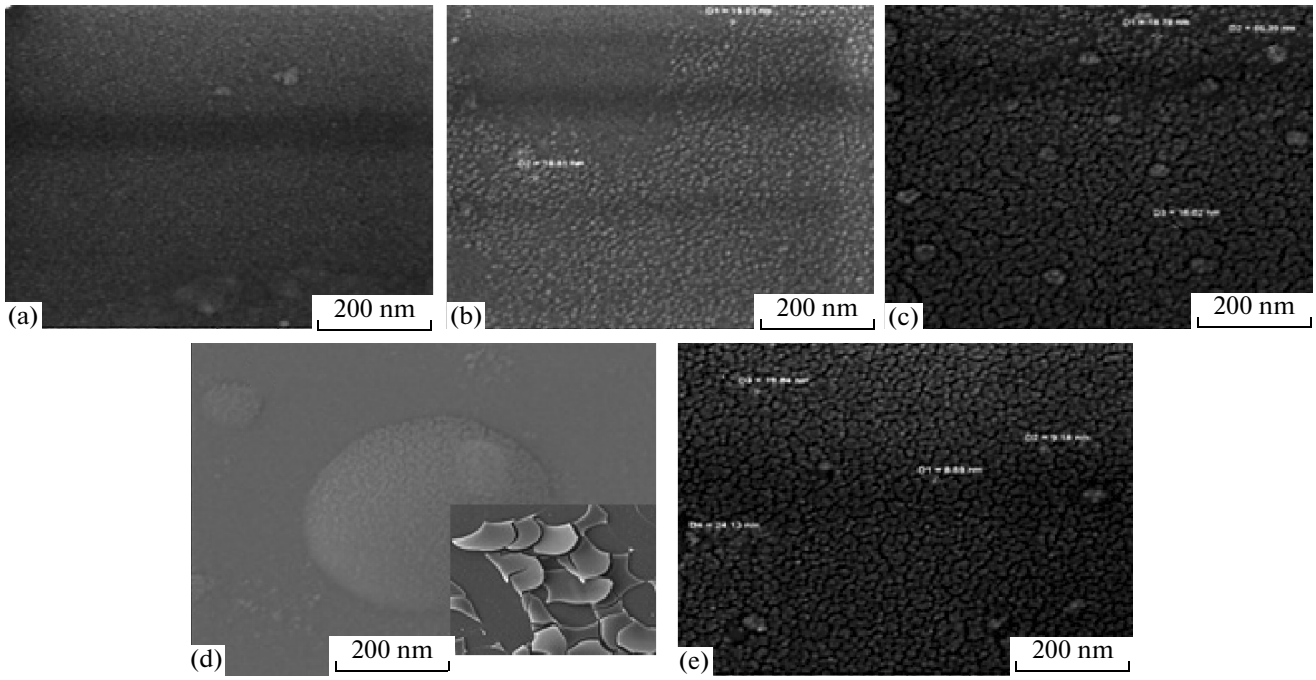

Fig. 5. Morphology of (a) *sn*, (b) *sp*, (c) *tp*, (d) *ts-p*, (e) *tsts-p* coatings.

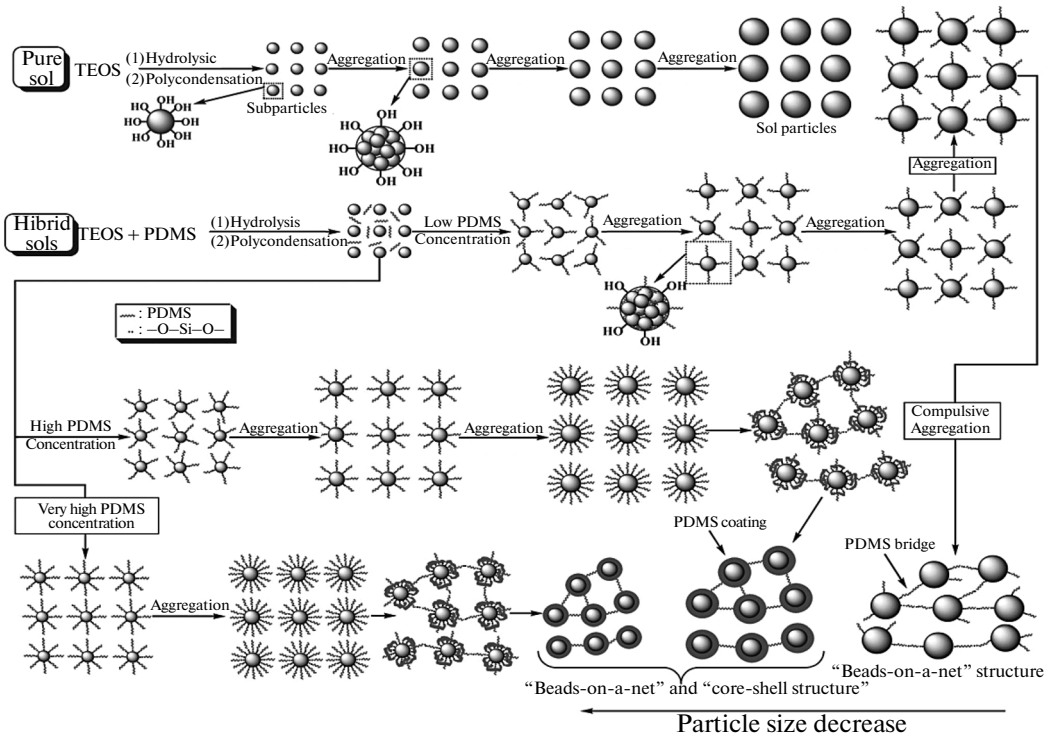

Fig. 6. Schematic representation of the particle growth process of pure and PDMS-containing silica sols [14].

with increasing surface density and thickness [17] as seen in Sn coating. Multilayer coatings were produced with the same refractive index and thickness of single layers.

Some of the best coverage of transmission after transmission of 150 days were re-evaluated and observed in Fig. 4. The results showed that after 150 days, *s-p* and *tsts-p* coatings do not show any loss of light, but the coatings *tststs-n* and *ts-p* have been reduced transmission by almost 2%. The presence of triton in *tststs-n* leads to loss of light. In this instance, the amount of light due to the presence of hydrophobic polydimethyl siloxane and absence of hydrophilic triton was high. A hydrophobic solution has its role to play well and as barrier coatings for adsorbed contamination environment and thereby stabilize the amount of light passing through them.

Microscopic images of the coatings can be seen in Fig. 5. Silica containing triton coatings pictures represent a coherent structure with the fine particles and pores. However; without triton example, silica particles are bigger and more spread. The triton additive in the coating has been efficacious.

In all coatings, PDMS began to react with hydroxyl groups on the surface of the silica particles. PDMS acts as a bridge between the silica particles and the resulting beads-on-a-net structure as shown in Fig. 6, is achieved. The formation of this structure significantly increases the viscosity of the sol [14]. These structures can be seen in the coatings. Single-layer titania coating showed agglomerated surface. The small size of titania particles are active and tend together. Agglomerated particles approximately 60 nm and smaller particles are about between 10–20 nm. The multilayer coatings in the transmission were evaluated microscopically. In two layer mode, titania-silica surfaces were uneven. Part of the observed surface scaling and in the other part blistering was observed. No uniformity of the coating leads to decrease transmission during the time. The titania-silica coating with four layers is uniform and it is almost like titania single layer. More compact and nanopores coatings cause to increment transmittance.

CONCLUSION

On the basis of this report, stacks of high quality coatings of titania, silica and/or multilayer silica and titania containing PDMS binder can be reproducibly deposited by a sol–gel dip coating process. Results showed, a combination of triton and PDMS materials in coatings haven't favorable antireflective property and for existence hydrophilic triton don't durable with time. But without triton containing coatings are more durable and 4th titania-silica-titania-silica coating shows high transmittance about 98%. Finally, alternating stacks of low and high refractive materials SiO_2

and TiO_2 containing PDMS is approached for more than one wavelength which increases the spectral bandwidth and has more lifetimes.

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