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ABSTRACT

Thin films on glazing play an important role in the design of solar energy conversion systems as thermal collectors or photovoltaic panels. Antireflective coatings based on porous silicon dioxide are well established in the field of solar collector glazing. Regarding architectural integration of thermal collectors, colored glass panes based on multilayer interference stacks of dielectric thin films offer a smart alternative to the coloration of the absorber sheets. Materials with tunable refractive index are highly desirable in such coatings in order to give access to optimised designs.

Thin films of silicon titanium mixed oxides $Ti_xSi_{1-x}O_2$ have been deposited in a particle free atmosphere by a sol-gel dip-coating process. Optical properties of thin films have been characterized by spectrophotometry and spectral ellipsometry. A nanocomposite structure has been evidenced by Transmission Electron Microscopy (TEM).

As low tunable refractive index material, novel nanocomposite thin films based on the elements Mg, F, Si and O have been deposited. Transparent and homogenous thin layers were achieved with variable Mg:Si molar ratios. Surprisingly low refractive index values have been found, reaching desired values for anti-reflective applications. Broad spectral transmittance maxima are observed with values up to 99.8 %. The nanostructure of quaternary Mg-F-Si-O thin films has been investigated by TEM, showing evidence of embedded crystalline nanoparticles. In comparison to existing anti-reflective materials, the novel quaternary thin films might be highly interesting regarding improvement of hardness and improved aging stability with respect to pores filling by hydrocarbons.

Intermediate size A4 colored glazing based on $Ti_xSi_{1-x}O_2$ films have been produced exhibiting 14.0 and 12.6 % visible reflectance and only small energy losses (1.4 and 3.4 % with respect to the uncoated substrate) showing the high potential of such materials for colored solar facades. A real-sized prototype of colored thermal solar collector has been realized, providing a convincing demonstration device.

INTRODUCTION

Increasing interest for multifunctional active solar facades providing daylight, heat and electricity [1] calls for the development of glazing specifically designed to deal with both energetic requirements and architectural integration. Thin films on glazing, such as antireflective coatings of porous silicon dioxide [2], are widely used in solar energy conversion systems. Colored glass panes based on dielectric thin films multi-depositions have been demonstrated to be of special interest for thermal solar collectors [3]. The optimisation of the optical properties of such coatings might be greatly improved by the use of materials with tunable and/or low refractive index [4]. Intermediate behaviours are typically obtained by mixing two components with high and low refractive index, the resulting properties being theoretically predicted by the effective medium theories (EMTs) [5]. Brinker and al. reported about the fabrication of antireflective thin films based on mixed oxide $Ti_xSi_{1-x}O_2$ [6]. Porous SiO_2 and magnesium difluoride MgF_2 (refractive index approx. 1.38) are commonly used as low refractive index coatings [7]. Long term durability of these materials is a critical issue, especially in regard to the mechanical stability of porous films and hardness of MgF_2 thin films. Sol-gel deposition of magnesium fluoride is not widespread, principally due to the difficulty to work with fluorine containing chemicals like hydrofluoric acid (HF). Fujihara and al. have developed a synthesis based on trifluoroacetic acid, making handling easier [8]. To overcome difficulties presented by sol-gel MgF_2 and porous SiO_2 thin films, Rywak and al. proposed to immerse nanocrystals of magnesium difluoride in an amorphous SiO_2 matrix but no optical measurements were provided [9]. Expected properties of this material would be an intermediate varying refractive index and increased mechanical resistance due to compact silicon dioxide density. The aim of this work is to present sol-gel silicon titanium mixed oxides and quaternary Mg-F-Si-O nanocomposite thin films for solar glazing applications such as antireflective glass and colored panes with optimised energetic transmission.

EXPERIMENT

Samples preparation

Sol-gel $Ti_xSi_{1-x}O_2$ solutions were obtained by mixing in appropriate concentrations Si and Ti containing solutions. Tetraethyl orthosilicate (TEOS, $C_8H_{20}O_4Si$) was diluted in ethanol and hydrolysed by stirring during 30 minutes at 60°C to prepare a silicon based sol-gel solution. The Ti solution was obtained by careful hydrolysis of tetraisopropyl orthotitanate (TIOT, $C_{12}H_{28}O_4Ti$) diluted in ethanol in presence of nitric acid (HNO_3 at 65 %) and by heating at 40°C. Triton x-100 was added to improve wettability during the deposition process.

Sol-gel solutions containing respectively Si and Mg-F were prepared separately before being mixed at desired molar ratio for the synthesis of quaternary Mg-F-Si-O films. The solution containing Si was obtained by hydrolysing TEOS during two hours at 50°C in presence of nitric acid using ethanol as solvent. Trifluoroacetic acid (TFA, $C_2HF_3O_2$) and magnesium acetate tetrahydrate ($C_4H_6O_4Mg\cdot4H_2O$) were dissolved either in ethanol or isopropanol for the synthesis of Mg-F solutions. The hydrolysis step was completed by addition of water and by stirring during two hours at 25°C. Two sets of solutions were obtained by mixing Si and Mg, F solutions in appropriate molar ratio: purely ethanol based (solutions A) or mixed ethanol-isopranol based (solutions B) solutions. Triton-x-100 was added to both sets of solution.

Dip-coating experiments were carried out with an apparatus specially designed to achieve a vibration-free and regular movement for the dipping and withdrawal of the substrates. The description of the apparatus has been given previously elsewhere [10].

Substrates consisting of microscope slides glass or A4-sized glass panes were cleaned in a laboratory dish washer and rinsed with demineralised water. Thin films prepared for ellipsometric measurements and TEM investigations were deposited on monocrystalline silicon wafers. A pre-deposition treatment of the wafers consisting in heating at 850°C during 4 hours was applied. The resulting 30 nm depth oxidation has been shown to improve the adhesion between the substrate surface and deposited thin xerogel films. After deposition, samples were transferred in an oven and heated at 400°C during one hour in air.

Measurements

A grating spectrometer (ORIEL MS 125TM 1/8m Spectrograph, with an Intaspec TM II Photodiode Array Detector and sighting optics) have been employed to measure the spectral transmittance of thin films in the visible range (380-780 nm). The precision of the measurements has been estimated between 0.3 to 0.5 percentage points. Measurements of thin films refractive index and thickness have been performed in the UV-VIS range (300- 820 nm) by a spectroscopic ellipsometer (SOPRA GESP5). Solar transmittance has been measured by a thermopile detector with a constant spectral sensitivity (ORIEL 70260) using a solar simulator (ORIEL 66902 with 150 Watts Xenon arc lamp) as light source. The nanostructure of the thin films has been investigated on a Philips CM20 Transmission Electron Microscope (TEM). Cleaved edge and cross sectional samples have been prepared.

RESULTS AND DISCUSSION

Mixed oxides thin films characterization

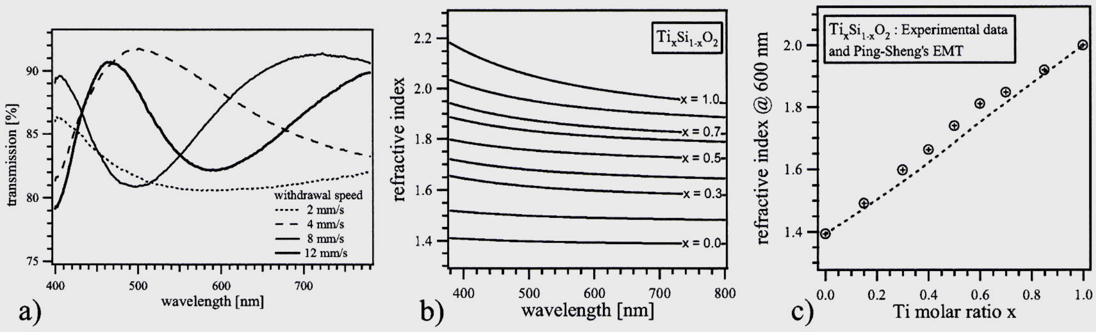
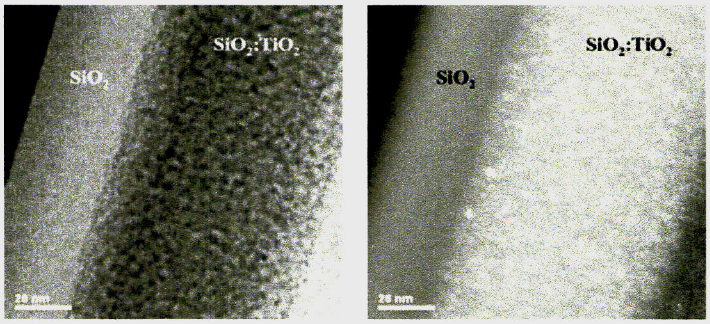


Figure 1: a) Spectral transmittance of $Ti_{0.5}Si_{0.5}O_2$ samples with variable withdrawal speed b) Dispersion relations n(λ) measured by spectral ellipsometry for variable stoichiometry c) Refractive index values at λ = 600 nm versus Ti concentration (markers) and comparison with Ping-Sheng EMT predictions (dotted line).

Highly homogenous and defect-free mixed oxides thin films have been deposited with variable Ti:Si molar ratio ranging from pure SiO_2 to pureTiO_2. Samples approximately 30 to 200 nm thick have been obtained by changing the withdrawal speed (v_t) during the dip-coating process. The spectral transmission has been measured for each concentration and for variable thickness. Figure 1a) presents results for $Ti_{0.5}Si_{0.5}O_2$ films on glass substrates, showing transmittance maxima exceeding 90 %. Refractive indices measured by spectral ellipsometry are shown in figure 1b). As expected, dispersion relations n(λ) for mixed oxides exhibit intermediate values between silica (n approx. 1.4) and titanium dioxide (n approx. 2.0). Values at λ = 600 nm versus Ti concentration have



a) b)

Figure 2: TEM images of a cross section of a $Ti_{0.5}Si_{0.5}O_2$ film on preoxidized silicon wafer: a) bright field b) dark field imaging mode.

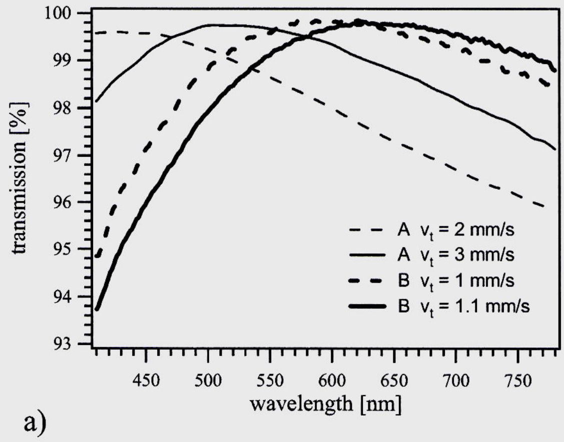
been plotted in figure 1c) and compared to Ping-Sheng effective medium calculations [5] showing good agreement between experimental data and theoretical predictions. Evidence for a granular structure on the nanometer-scale has been found by TEM investigations. Figure 2a) shows a bright field image of the cross section of a $Ti_{0.5}Si_{0.5}O_2$ nanocomposite film deposited on a preoxidized silicon wafer. Titanium-rich regions appear here as dark grains becoming bright points when observed in the dark field imaging mode (figure 2b)). These observations strongly suggest the presence of TiO_2 nanocrystals embedded in an amorphous SiO_2 matrix.

Characterization of quaternary Mg-F-Si-O thin films

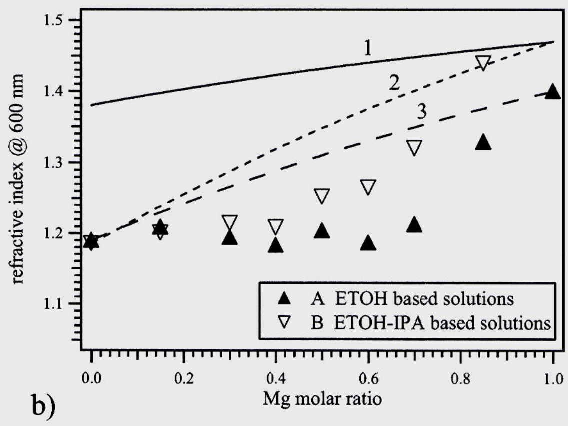
Homogeneous transparent thin films with variable Mg:Si molar ratio and thickness have been achieved by deposition on glass substrates starting from solutions A and B. Spectrophotometric measurements of normal transmittance on a large set of samples have shown broad spectral maxima exceeding 99.5 % for Mg:Si molar ratios ranging from 30:70 to 60:40. Transmittance spectra of equal Mg:Si molar ratio thin films on glass are shown as example in figure 3a). Using transmittance spectra data and measured refractive index in the visible range, total solar transmission has been predicted by extrapolation for a 114 nm thick sample exhibiting a maximum of 99.8 % centred at 571 nm: a value higher than 97 % was obtained.

The refractive index n of Mg-F-Si-O thin films with variable thickness and composition has been determined in the UV-VIS range by spectral ellipsometry. Surprisingly low refractive index values have been found. Values at 600 nm versus composition are plotted in figure 3b) for samples deposited with the same withdrawal speed. For thin samples (< 100 nm) n ranges from 1.2 to 1.25 for high Mg concentrations, reaching desired values for anti-reflection applications. Ping-Sheng effective medium calculations have been performed based on different assumptions on mixed components (figure 3b), curves 1, 2 and 3). Curve 1 has been established on the hypothesis of a two components system containing MgF_2 (n_{bulk} = 1.38) and SiO_2 (n_{bulk} = 1.47), excluding an eventual third phase or any porosity. Extreme refractive index values from experimental data have been used to establish curves 2 and 3 for samples issued from solutions B and A respectively. Strong deviations are noticed in all cases.

First investigations by TEM have shown embedded nanocrystallites, suggesting a two-phase system.



a)



b)

Figure 3: a) Transmittance spectra of equal Mg:Si molar ratio thin films based on solutions A and B with variable withdrawal speed (v_t) b) Refractive index at λ = 600 nm for variable Mg:Si molar ratio measured by spectral ellipsometry (triangles) and effective medium calculations (curves 1, 2 and 3).

A4-sized mixed oxides colored glazing

A large freedom in the design of multilayer coatings is provided by nanocomposite mixed oxides due to their tunable refractive index. Two colored glazing have been realised on A4-sized glass panes (4 mm thick, solar transmission 89.4 %) by cycling dip-coating and thermal treatment steps. Following simulations of optical behaviour, two designs consisting of 3-layered superpositions of SiO_2 and $Ti_{0.3}Si_{0.7}O_2$ with both sides of the glass coated have been selected. Samples obtained are shown in figure 4: an orange-brownish (on the left) and a blue glazing (on the right). The diminution in the solar transmittance with respect to the uncoated glass is only 1.4 and 3.4 percent points for the blue and the orange-brownish sample respectively. The spectral reflectance is given in figure 5, yielding a visible reflectance of 14 % (blue sample) and 12.6 % (orange-brownish sample).

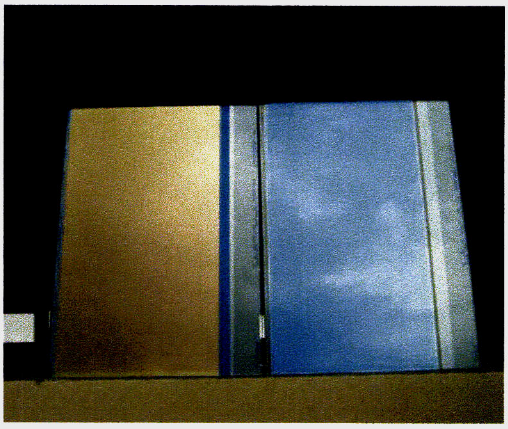


Figure 4: Orange-brownish (left) and blue (right) A4-sized multilayered colored glazing based on mixed oxides thin films.

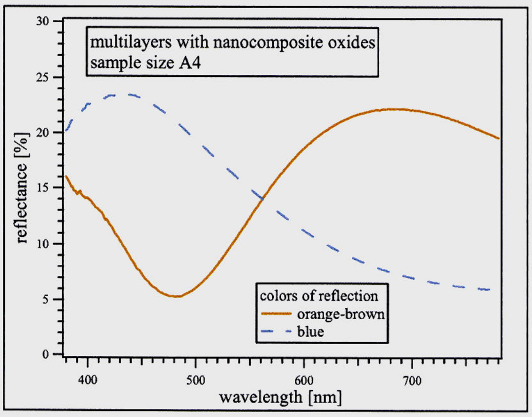
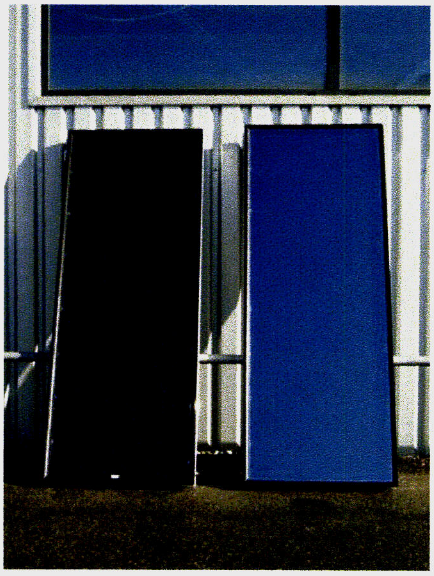


Figure 5: Spectral reflectance of blue and orange-brownish samples.

Prototype of colored collector glazing

A prototype of colored glazing on large panes of solar glass (dimensions 1.90 m x 3 m) has been prepared by magnetron sputtering with the collaboration of the company GLAS TRÖSCH, Switzerland. A selected design of coatings was optimised to deliver a light blue reflectance with an expected solar transmission T_{sol} = 81 % for a visible reflectance R_{vis} = 25 %. The glazing was cut and installed on a real-sized solar collector (AZUR20, AGENA, dimensions 0.93 m x 2.43 m), demonstrating its high potential of concealing the absorber and showing a great stability with respect to a variation of the angle of reflection (see figure 6).

Figure 6: Solar collectors covered equipped with a conventional collector glazing (on the left) and with the novel blue-colored coated solar glazing glazing (on the right).



CONCLUSIONS

Nanocomposite thin films of mixed oxides and fluorides-oxides materials have been prepared by sol-gel dip-coating. The existence of very promising optical properties of such coatings has been demonstrated in regard to solar glazing applications. Concerning designs of colored glazing, tunable refractive index of $Ti_xSi_{1-x}O_2$ has been proved highly useful for the optimisation of the solar transmission and visible reflection. Interesting anti-reflective behaviours resulting from the low refractive index of the Mg-F-Si-O films should find promising opportunities in the development of new solar glazing. The feasibility at industrial scale of colored glazed solar collectors has been demonstrated by the preparation of a blue prototype, highlighting the important energetic and architectural potential of such devices for active solar facades.

ACKNOWLEDGEMENTS

Financial support of this work has been provided by the Swiss Federal Office of Energy SFOE. Authors are especially thankful to GLASS TRÖSCH and AGENA for collaboration on the realisation of an industrial collector prototype. The authors would like to thank Prof. L. Zuppiroli, M. Schär and R. Ferrini from the LOMM (EPFL) for access to ellipsometry facilities and for their valuable support. Authors are grateful to L. Deschamps for software development and to P. Loesch for technical support.

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INTRODUCTION

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EXPERIMENT

Samples preparation

Sol-gel $Ti_xSi_{1-x}O_2$ solutions were obtained by mixing in appropriate concentrations Si and Ti containing solutions. Tetraethyl orthosilicate (TEOS, $C_8H_{20}O_4Si$) was diluted in ethanol and hydrolysed by stirring during 30 minutes at 60°C to prepare a silicon based sol-gel solution. The Ti solution was obtained by careful hydrolysis of tetraisopropyl orthotitanate (TIOT, $C_{12}H_{28}O_4Ti$) diluted in ethanol in presence of nitric acid (HNO_3 at 65 %) and by heating at 40°C. Triton x-100 was added to improve wettability during the deposition process.

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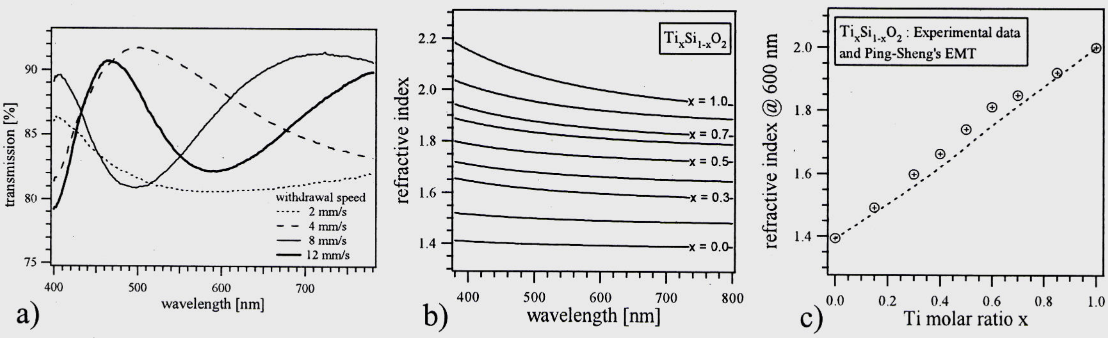
RESULTS AND DISCUSSION

Mixed oxides thin films characterization



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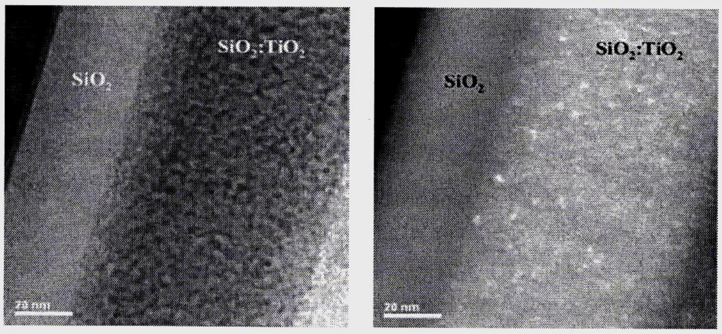

a) b)

Figure 2: TEM images of a cross section of a $Ti_{0.5}Si_{0.5}O_2$ film on preoxidized silicon wafer: a) bright field b) dark field imaging mode.

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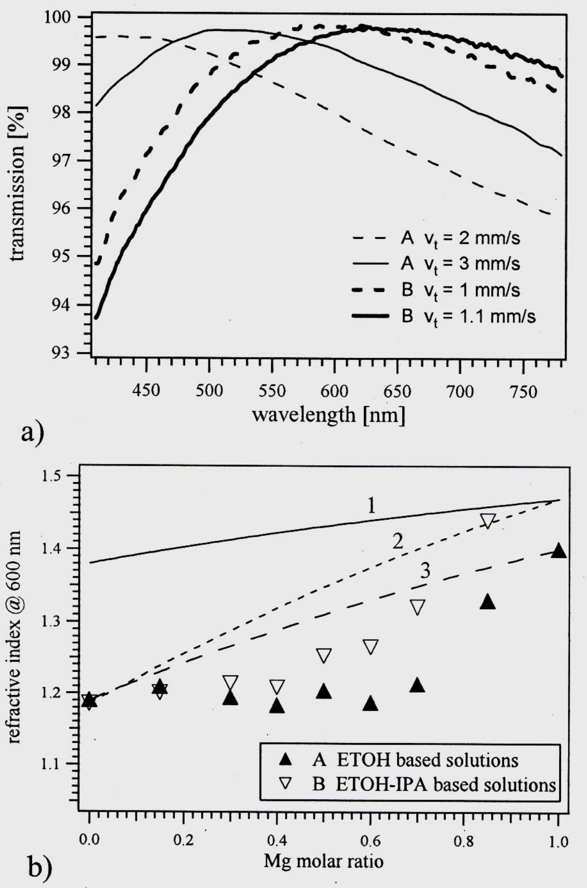

Figure 3: a) Transmittance spectra of equal Mg:Si molar ratio thin films based on solutions A and B with variable withdrawal speed (v_t) b) Refractive index at λ = 600 nm for variable Mg:Si molar ratio measured by spectral ellipsometry (triangles) and effective medium calculations (curves 1, 2 and 3).

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First investigations by TEM have shown embedded nanocrystallites, suggesting a two-phase system.

A4-sized mixed oxides colored glazing

A large freedom in the design of multilayer coatings is provided by nanocomposite mixed oxides due to their tunable refractive index. Two colored glazing have been realised on A4-sized glass panes (4 mm thick, solar transmission 89.4 %) by cycling dip-coating and thermal treatment steps. Following simulations of optical behaviour, two designs consisting of 3-layered superpositions of SiO_2 and $Ti_{0.3}Si_{0.7}O_2$ with both sides of the glass coated have been selected. Samples obtained are shown in figure 4: an orange-brownish (on the left) and a blue glazing (on the right). The diminution in the solar transmittance with respect to the uncoated glass is only 1.4 and 3.4 percent points for the blue and the orange-brownish sample respectively. The spectral reflectance is given in figure 5, yielding a visible reflectance of 14 % (blue sample) and 12.6 % (orange-brownish sample).

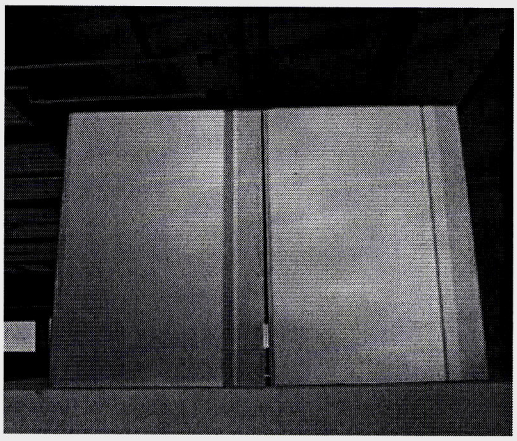

Figure 4: Orange-brownish (left) and blue (right) A4-sized multilayered colored glazing based on mixed oxides thin films.

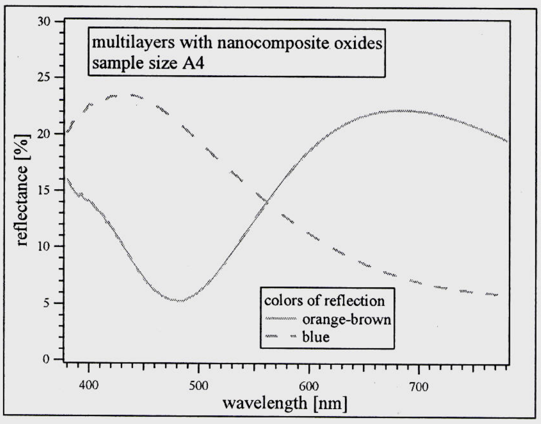

Figure 5: Spectral reflectance of blue and orange-brownish samples.

Prototype of colored collector glazing

A prototype of colored glazing on large panes of solar glass (dimensions 1.90 m x 3 m) has been prepared by magnetron sputtering with the collaboration of the company GLAS TRÖSCH, Switzerland. A selected design of coatings was optimised to deliver a light blue reflectance with an expected solar transmission T_{sol} = 81 % for a visible reflectance R_{vis} = 25 %. The glazing was cut and installed on a real-sized solar collector (AZUR20, AGENA, dimensions 0.93 m x 2.43 m), demonstrating its high potential of concealing the absorber and showing a great stability with respect to a variation of the angle of reflection (see figure 6).

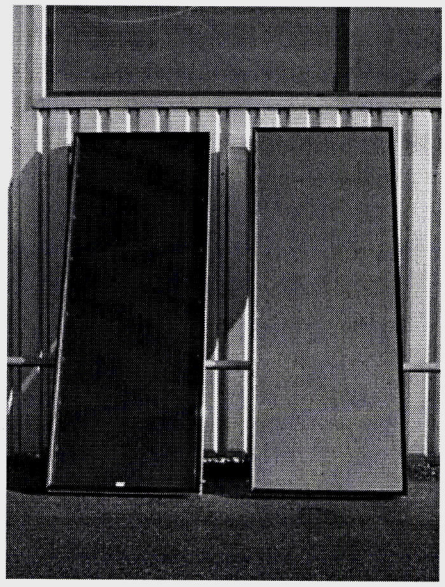

Figure 6: Solar collectors covered equipped with a conventional collector glazing (on the left) and with the novel blue-colored coated solar glazing glazing (on the right).

CONCLUSIONS

Nanocomposite thin films of mixed oxides and fluorides-oxides materials have been prepared by sol-gel dip-coating. The existence of very promising optical properties of such coatings has been demonstrated in regard to solar glazing applications. Concerning designs of colored glazing, tunable refractive index of $Ti_xSi_{1-x}O_2$ has been proved highly useful for the optimisation of the solar transmission and visible reflection. Interesting anti-reflective behaviours resulting from the low refractive index of the Mg-F-Si-O films should find promising opportunities in the development of new solar glazing. The feasibility at industrial scale of colored glazed solar collectors has been demonstrated by the preparation of a blue prototype, highlighting the important energetic and architectural potential of such devices for active solar facades.

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