



Colored Solar Collectors

Phase II : From laboratory samples to collector prototypes

Final Report

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author and coauthors	Dr. Andreas Schüler, Christian Roecker Estelle De Chambrier, MariaCristina Munari Probst
institution	Ecole Polytechnique de Lausanne EPFL Laboratoire d'Energie Solaire et de Physique du Bâtiment LESO-PB
address	Bâtiment LE, 1015 Lausanne
phone, email, webpage	(021) 693 43 41 christian.roecker@epfl.ch (021) 693 4544, andreas.schueler@epfl.ch http://lesowww.epfl.ch
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SUMMARY

The architectural integration of glazed thermal solar collectors into buildings facades is limited by several factors: limited dimensional freedom, limited jointing choice and above all the black color and surface irregularities of the absorber visible behind collector glazing. Unlike for the two first factors that can be handled by industry, color is more complex. A certain freedom in color choice would be desirable, but the colored appearance should not cause an excessive degradation of the collector efficiency. Multilayered interference filters on the cover glass can produce an energy-efficient colored reflection, hiding the corrugated metal sheet, while transmitting the non-reflected radiation entirely to the absorber. These interference filters are designed and optimized by numerical simulation, and are manufactured by sol-gel dip-coating or magnetron sputtering.

Nanocomposite and nanoporous thin films are perfectly suited for the considered application. Due to the tunability of the refractive index, nanostructured materials such as $\text{SiO}_2/\text{TiO}_2$ composites and porous SiO_2 are very useful for application in multilayer interference stacks. Novel quaternary Mg-F-Si-O films exhibit a surprisingly low refractive index and are therefore promising candidates for highly transparent coatings on solar collector glazing. The nanostructure of these thin films is studied by transmission electron microscopy, while the optical constants are measured precisely by ellipsometry.

For a convincing demonstration, sufficiently large samples of high quality are imperatively needed. The sol-gel deposition of the multilayered coatings on A4 - sized glass panes has been demonstrated in the laboratory by EPFL-LESO. The produced coatings exhibit a colored reflection in combination with a high solar transmittance, a homogenous appearance, and are free of visible defects. Film hardening by UV exposure will result in speeding up the sol-gel process and saving energy, thereby reducing costs significantly.

In collaboration with industry, real scale glass panes are coated with the novel multilayers. The novel glazing is integrated into first prototype collectors.

The necessary characteristics needed to successfully integrate solar collectors into facades have been thoroughly studied and published. Combined with selected interference filters colors, the various possible diffusing treatments have been studied and tested both on A4 size samples and on real size collector glasses. One major advantage of the new glazing has been shown, namely the possibilities opened by the use of the same glass for collectors and insulation cladding. Feedback collected from architects and other users has demonstrated the great interest for the architectural possibilities offered by this new glazing.

Project Goals

Architectural integration of solar energy systems into buildings has become a widely recognized issue, which regards techniques ranging from photovoltaics and daylighting to thermal solar energy conversion. Thermal solar collectors, typically equipped with black, optical selective absorber sheets, exhibit in general good energy conversion efficiencies. However, the black color, and sometimes the visibility of tubes and unwanted undulations of the thin metal sheets, limit the architectural integration into buildings. A recent opinion poll [WEI01] showed that 85% of architects would prefer other colors than black, even if a lower efficiency was the price to pay.

Several research groups have proposed to color the absorber sheets. This can be obtained by modifying the process parameters used for the production of black selective absorber coatings. An alternative approach is to establish a colored reflection not from the absorber but from the collector glazing [SCH03]. Interference colors of dielectric thin films are ideally suited for this purpose. Multilayered interference filters on the cover glass can produce an energy-efficient colored reflection, hiding the corrugated metal sheet, while transmitting the non-reflected radiation entirely to the absorber. These interference filters are designed and optimized by numerical simulation, and are manufactured by sol-gel dip-coating or magnetron sputtering. Due to the possibility of tailoring the optical properties of nanostructured materials, nanocomposite and nanoporous thin films are perfectly suited for the considered application. Novel coatings shall be developed on the laboratory scale, then fabricated first on an intermediate size scale (A4) for demonstration, and finally on the industrial scale. Collector prototypes shall be obtained. The exciting new possibilities for architectural integration of the novel solar collectors shall be studied.

Approach :

1. Infrastructure for sol-gel deposition of multilayers on A4 - sized substrates

For a convincing demonstration sufficiently large samples of high quality are imperatively needed. First colored multilayers on A4 sized glass substrates shall be manufactured in the laboratory, requiring:

- an infrastructure for sample handling and dip-coating
- an optimization of the cyclic process for multilayer deposition

2. Methodology of optical measurements

For a controlled sol-gel deposition of multilayers, the optical properties of the thin film materials have to be known precisely. The optical performance of the novel glazing has to be characterized accurately. The methods include:

- for determination of optical constants: spectrophotometry and ellipsometry
- for the quantification of colors: colorimetry
- for the measurement of the solar transmittance: global method for non-diffusing samples with solar simulator & thermopile

3. Sol-gel deposition of nanostructured titanium silicon oxide films ($\text{Ti}_{1-x}\text{Si}_x\text{O}_2$)

Nanocomposite $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ thin films shall provide a large range of refractive indices. Suitable precursor solutions for the deposition of such nanocomposite films have to be developed. Multilayered coatings with a high energy efficiency of the colored reflection shall be designed and prepared by cyclic sol-gel dip-coating.

4. Thin film materials with low refractive index (low-n materials)

The availability of thin film materials with a refractive index lower than that of silicon favors a higher solar transmission at a given value of visible reflectance.

The feasibility of the sol-gel deposition of the following materials shall be studied:

- porous SiO_2
- MgF_2
- novel fluoride/oxide nanocomposite thin films (quaternary Mg-F-Si-O films)

The optical constants of those low refractive index materials shall be determined precisely.

5. Film hardening by UV-curing

For the industrial production of multilayers by the sol-gel process, UV-curing shall replace the thermal annealing step needed after the deposition of each individual layer. Film hardening by UV exposure will result in speeding up the process and saving energy, thereby reducing costs significantly.

The experimental infrastructure for UV-curing shall be established, including the construction of a suitable UV source and the installation of UV screening panels (safety precautions). The used precursor solutions shall be modified in order to achieve a photosensitization yielding film hardening by photopolymerization.

6. Demonstration of sol-gel deposited samples (substrate size A4)

A model collector for demonstration of the A4-sized sol-gel samples shall be built and presented to architects, facade manufacturers and glass industry.

7. Prototype fabrication of colored collector glazing on the industrial scale by magnetron sputtering (substrate size 1.90 m x 3 m)

The fabrication of prototype glazing on the real scale is essential for a convincing demonstration of the novel solar collectors.

An industrial partner for the prototype fabrication of colored collector glazing shall be found. The possibilities and limitations of eventually existing production lines shall be discussed, and adapted multilayer designs shall be proposed according to the given boundary conditions. Real scale glass panes shall be coated with the novel multilayers, and the novel glazing shall be integrated into first prototype collectors.

8. Architectural integration of the novel colored solar collectors

Three main activities were planned in this topic:

- develop the potential of the new glazing by investigating all the possible glass treatments for the diffusing layer, including patterns and text tests. Select most suited colors for façade use.
- explore the necessary architectural conditions needed to fully exploit the new glazing, with dimensional flexibility, material appearance and jointing being key issues. Explore the possibilities opened by the use of the same glass for collectors and insulation cladding.
- prepare demonstration material to evaluate the potential of various combinations, Get feedback by interviewing architects and collector manufacturers. Spread the information in exhibitions and conferences.

Description of Work and Results

1. Infrastructure for sol-gel deposition of multilayers on A4 - sized substrates (size A4)

One of the technical challenges of the project is related to the fact that in order to provide convincing samples for demonstration it is absolutely necessary to have coatings of high quality. It shall be shown that colored multilayered coatings can be manufactured in a satisfying quality by the sol-gel dip-coating process. Important factors for the quality of the coatings are particle-free solutions, the vibration free movement during sample withdrawal from the solution, and the protection from dust during dip-coating and repeated thermal annealing.

4.1 Dip-coating

The dip-coater developed by EPFL-LESO provides a vibration-free and regular movement for the dipping and withdrawal of the substrates. A computer drawing of the dip-coater is shown in Fig.1. A servo drive (MKD 25B REXROTH) is controlled by a feedback loop (control unit Ecodrive 03 REXROTH INDRAMAT). The speed of the rotation is adapted by a Neugart transmission and transformed into a translational movement by a helix equipped with a special ball bearing (compact module CKK 12-90, REXROTH). A microcomputer is used to command the control unit of the servo drive. For dust-protection the dip-coater is placed in a laminar flux chapel (SKANAIR VFC 120). The air quality is monitored by real-time particle counting (KLOTZ PSSair with isocinetic nozzle). In the laminar flux chapel typically less than 1 particle larger than 0.3 micron is counted per cubic foot (for comparison: ambient laboratory air: $\sim 10^4$ particles per cubic ft). After dip-coating, the resulting thin xerogel films have to be annealed typically at temperatures ranging from 250°C - 450°C.

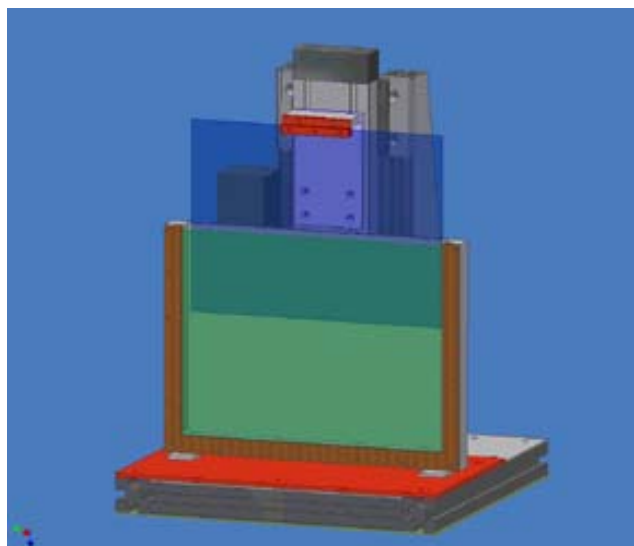


Fig.1: CAD model of the dip-coater developed by EPFL-LESO. The apparatus provides a vibration-free and regular movement for the dipping and withdrawal of the substrates. For dust-protection the dip-coater is placed in a laminar flux chapel.

4.2 Sample transfer and handling

For dip-coating, substrates have to be free of dust and grease. In order to ensure a high level of substrate cleaning, a professional laboratory dishwasher has been installed. Residual free cleaning by deionised water can thus be provided. A rack has been built for the A4 sized substrates, holding the glass panes during washing and drying.

Special reservoirs allow dip-coating of the A4 sized substrates. In order to keep the quantity of needed precursor solution low, the reservoirs are narrow but can be opened laterally for easy cleaning.

During the annealing step following the dip-coating procedure, the samples have to be protected from the particles present in the ambient laboratory air. A special bake-out container has been constructed, fitting ten samples of the A4 size [see Fig.2(a)]. The recipient is charged in the particle-free atmosphere provided by the filtered laminar flow, closed and subsequently transferred to the oven. After annealing, the container is transferred back to the laminar flow chapel again, where a subsequent dip-coating step can take place. Dip-coater, sample rack and bake-out container just fit into the laminar flux chapel [see Fig.2(b)].

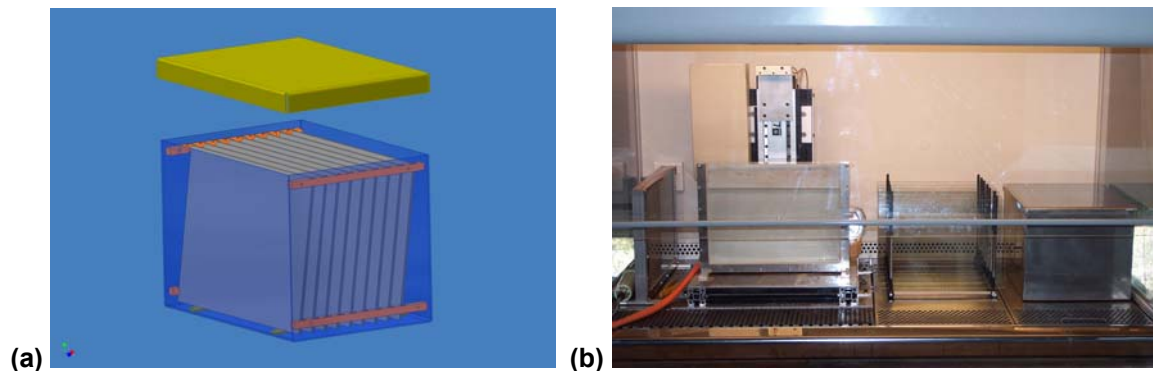


Fig.2: (a) Bake-out container for A4 sized samples. During the annealing step, samples remain under the protection from dust. (b) Laminar flux chapel with dip-coater, sample rack and bake-out container (from left to right).

4.3 Elaborating the process for high quality multilayer deposition

The preparation of defect-free homogenous multilayers requires an optimization of all aspects of substrate pretreatment, sample processing and handling.

The complete process includes:

- substrate washing with detergent, neutralisation step and subsequent rinsing cycles with deionised water
- transfer to laminar flow chapel
- mounting of substrate, removal of dust particles by anti-static brush or filtered nitrogen jet
- dip-coating (interruption of laminar flow for homogenous solvent evaporation)
- dissolution of excess gel on bottom edge of sample
- transfer to oven in closed bake-out container
- transfer back to laminar flow chapel
- subsequent dip-coating/annealing steps for multilayer formation

Fig.3(a) shows the glass panes during sol-gel processing in the drying rack. The resulting colored multilayered coatings are free of visible defects and exhibit a good homogeneity [see Fig.3(b)]. Various shades of color have been obtained by varying the withdrawal speed.

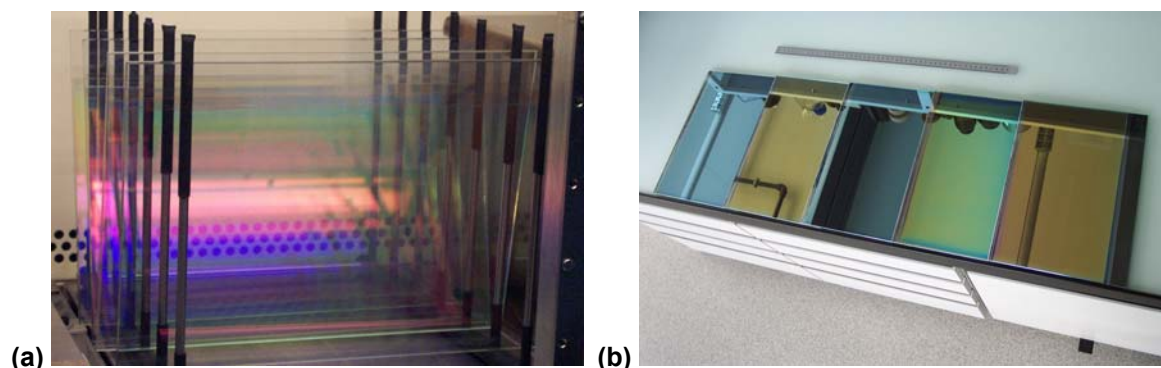


Fig.3: (a) Glass panes during sol-gel processing. (a) The resulting colored multilayered coatings are free of visible defects and exhibit a good homogeneity. Various color shades have been obtained by varying the withdrawal speed.

2. Methodology of optical measurements

For a controlled sol-gel deposition of multilayers, the optical properties of the thin film materials have to be known precisely. Spectrophotometry is used for the determination of the refractive index n and the extinction coefficient k . Spectroscopic Ellipsometry allows to infer those numbers with an even higher precision. Both methods are also used to establish the relation of film thickness and withdrawal speed for each precursor solution, which is essential for the controlled multilayer deposition by sol-gel dip-coating.

The quantification of the achieved colors, the color saturation, the angle-dependence and aging stability of the colors is provided by colorimetry, which is either based on measured reflectance or transmittance spectra or colorimetric devices working with three spectrally selective sensors.

The energy-efficiency of the colored reflection produced by the multilayered samples is characterized by the visible reflectance as determined by spectrophotometry, and by the solar transmission. For non-diffusing samples, the latter can be measured by a solar simulator in combination with a thermopile detector. The ratio of the visible reflectance and the solar energy losses serves hereby as a figure of merit.

2.1. Spectrophotometry

Spectral measurements are performed in the VIS/NIR range (380 nm to 950 nm) by a grating spectrophotometer (ORIEL MS 125TM 1/8m Spectrograph, with InstaspecTM II Photodiode Array Detector and sighting optics). An argon/mercury discharge lamp serves as wavelength standard for the calibration of the spectrophotometer.

A special sample holder for angle-dependent transmittance measurements has been assembled based on a precision rotary stage, which allows a very precise control of the transmission angle. The sample holder is aligned with the aid of a laser pointer and can be used in combination with a spectrophotometer (measurement of spectral transmittance) or with solar simulator and thermopile detector (direct determination of solar transmission).

An experimental setup for angle-dependent reflectance measurements has been designed and constructed. A special mechanism guarantees the alignment of sample, source, and spectrophotometer. The angular dependence of the color coordinates for the reflected light can be determined from the spectral data.

When a diffraction grating is used for spectrophotometry, it should be ensured that the measured signal is not perturbed by higher order diffraction. Order-sorting filters allow the suppression of such errors. In order to measure in a wide spectral range, two spectra are acquired from a thin film sample, with and without a red filter. Both spectra can then combined to yield reliable data, thus omitting the thermal noise due to the cut-off of the red filter (below 550 nm) and the contribution of the second order diffraction (above 700 nm).

For thick enough films, transmittance and reflectance spectra exhibit characteristic oscillations, which can be used to determine the refractive index at special wavelengths directly. The theoretical relation of the intensity difference between minima and maxima (ΔR) to the difference in refractive index (Δn) between substrate and film is illustrated in Fig.4(a). A value of the difference in refractive indices can be inferred directly for each position of either the reflection minima respectively the transmission maxima (in the case of n inferior for film than for substrate) or for each position of the reflection maxima respectively the transmission minima (in the case of n larger for the film than for the substrate). Since the refractive index of the glass substrate can be determined independently, this method yields precise values for the refractive index at the considered wavelengths.

The film thickness can then be determined by plotting the extrema positions vs. the number of the order j . From the slope s of the plot the film thickness d can be inferred by the relation $s = 1/(4nd)$. An example is shown in Fig.4(b). The positions of the minima and maxima have been extracted from a transmittance spectrum of a thin silicon oxide film on glass. The linearity of the graph confirms that the refractive index of the SiO_2 layer is rather constant.

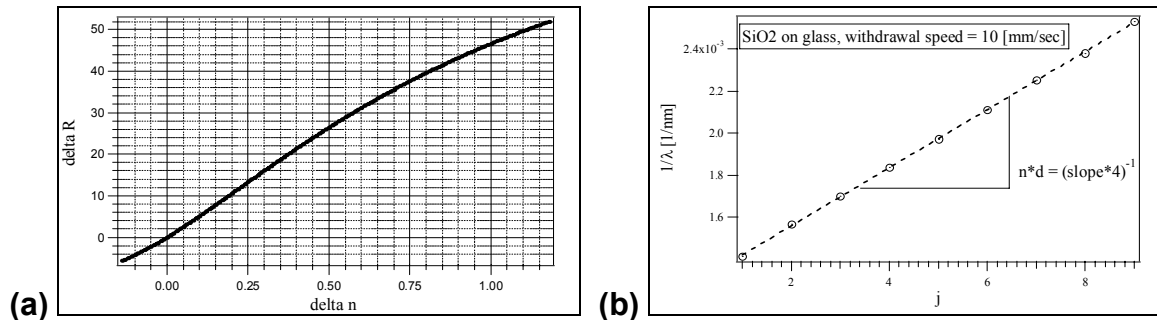


Fig.4: (a) Relation of the intensity difference of the minima and maxima in the transmittance or reflectance spectra to the difference in refractive indices of film and substrate. (b) Positions of maxima and minima in the transmission spectra of a SiO_2 film are plotted vs. the number of order j . The graph exhibits nearly perfect linear behavior. The slope of the plot yields a value for the optical path nd .

In the case where neither minima nor maxima are distinguishable in the measured spectra, the analysis should be based on angle-dependent spectra. For each wavelength, transmittance or reflectance values are acquired at different angles of incidence. The resulting curves can be used as target values for a numerical least square fit, yielding a value for the refractive index n at each considered wavelength. The obtained values can be interpolated by fitting a Cauchy dispersion formula to the data. The use of polarization filters allows to enhance the precision and the certainty of the method.

2.2 Spectroscopic ellipsometry

Spectroscopic ellipsometry is a precise optical measurement technique working with polarized light. The method compares the ratio of the reflection coefficients for parallel and perpendicular polarized light R_p and R_s . This relative measurement makes the technique independent from intensity fluctuations of the source, thus favoring a high precision. Output of the experiment are the ellipsometric angles Ψ and Δ , defined by the equation:

$$\tan(\Psi) \exp(i\Delta) = \frac{R_p}{R_s}$$

A scheme of the experimental configuration is shown in Fig.5. Linearly polarized light is incident on the sample (components parallel and perpendicular to the plane of incidence both non-zero). After reflection the polarisation will be in general elliptical, which is characterized by a detector behind a rotating analyzer, eventually in combination with a retarder (not shown in Fig.5). In spectroscopic ellipsometry, the use of a grating monochromator allows the acquisition of wavelength-dependent data.

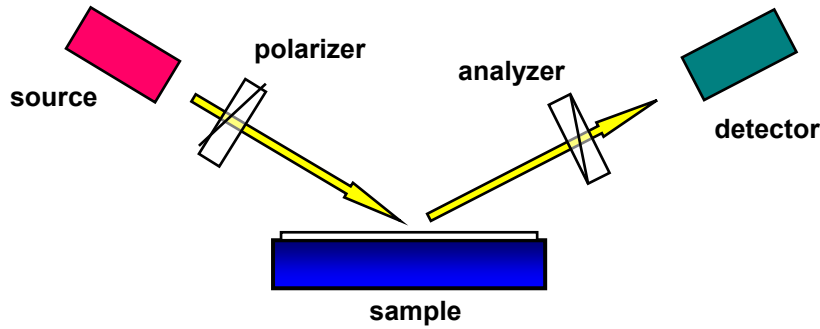


Fig.5: Scheme of ellipsometric measurements. After reflection of originally linearly polarized light the polarisation will be in the general elliptical, which is characterized by a rotating analyzer and a detector, eventually in combination with a retarder (not shown in the figure).

In order to infer the optical constants n and k and the thickness of thin film samples from the acquired spectra of Ψ and Δ , in many cases a function for the dispersion relation is assumed, for example a Cauchy dispersion relation:

$$n(\lambda) = n_0 + C_0 \frac{n_1}{\lambda^2} + C_1 \frac{n_2}{\lambda^4}$$

and

$$n(\lambda) = n_0 + C_0 \frac{n_1}{\lambda^2} + C_1 \frac{n_2}{\lambda^4}$$

with the wavelength λ and the constants n_i , k_i , $C_0 = 10^2$ and $C_1 = 10^7$. The numbers n_i , k_i can be used together with the film thickness d as parameters of a numerical fit to the experimental data.

Access to spectroscopic ellipsometers has been provided by the groups of Prof. Libero Zuppiroli at EPFL (instrument: SOPRA), and of Peter Oelhafen, University of Basel (instrument: SENTECH).

2.3 Colorimetry

A set of four reference samples has been investigated by two different methods, with a hand-held device based on a flash and three sensors (Minolta Cr-210b), and by acquiring spectra of the total hemispherical reflectance by means of the spectrometer (*ORIEL MS 125TM 1/8m Spectrograph, InstaspecTM II Photodiode Array Detector*) in combination with the integrating sphere (*Labsphere RT-060-SF/IG*). The CIE color coordinates x , y and Y have been calculated from the reflectance spectra. Fig.6 shows a comparison of the results for the CIE color coordinates x and y , as determined by the different methods (for an opening angle of 2° and the standard illuminant D_{65}). While there are no two methods agreeing perfectly, there is not any method yielding completely different results. The differences give an idea about the precision of this type of measurements, which is estimated to be in the order of ± 0.005 for x and y (± 0.04 and ± 0.06 , respectively), and in the order of ± 1.6 for Y .

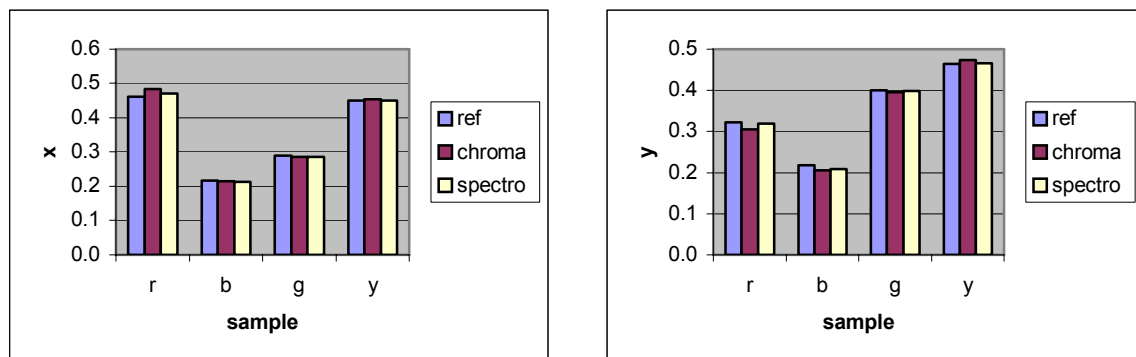


Fig.6: CIE color coordinates x and y , as determined for four reference samples (colors red, blue, green and yellow, denoted as r , b , g , y) by the Minolta instrument (chroma) and by the spectrophotometer with integrating sphere (spectro). The measured values are compared to the reference values provided by the manufacturer of the reference samples (ref). The differences give an idea about the precision of this type of measurements. While there are no two methods agreeing perfectly, there is not any method yielding completely different results.

2.4 Solar Simulator

A method of measuring directly the solar transmittance of non-diffusing samples has been established, based on a solar simulator and a thermopile detector with a constant spectral sensitivity.

Instruments:

Solar simulator: 150 Watt ozone free Xenon arc lamp in arc lamp housing *ORIEL 66902*

Radiant Power Meter: *ORIEL 70260*, with thermopile probe *70264* and fused silica filter *44950*

For terrestrial applications, the global solar spectrum at air mass 1.5 ("AM1.5g") is one of the most common choices as illuminant reference. Special filters are used to match the spectrum of the source to the desired solar spectrum.

Filter combination 1 : filters 81090, 81091 and 81094

Filter combination 2 : filters 81090 and 81092

For a set of given samples (multilayered thin oxide films on glass A-F), the solar transmission has been measured with the solar simulator and the radiant power meter, using the two different filter combinations. The obtained values have been compared to the data obtained by

spectrophotometry in Basel (*VARIAN Cary 5*). Filter combination 2 seems to be most suitable for this measurement. The deviations from the spectrophotometrically determined values amount only to approx. 1 %.

3. Sol-gel deposition of nanostructured titanium silicon oxide films ($\text{Ti}_{1-x}\text{Si}_x\text{O}_2$)

3.1 Synthesis of suitable precursor solutions and deposition of single layers

The solar transmission of multilayers based on individual layers of pure TiO_2 and pure SiO_2 can be improved if intermediate refractive indices are available (for corresponding simulations see ref. [3]).

The tunable refractive index of nanocomposite materials provides a large degree of freedom for an optimization of the coatings. By mixing silicon oxide ($n \approx 1.47$) and titanium oxide (for sol-gel films $n \approx 2.2$), any intermediate refractive index shall be achieved, opening manifold possibilities for multilayer design. Mixtures of silicon and titanium oxides shall thus be considered. The compatibility problems of the originally used precursor solutions (strong coagulation when mixing) have been solved by a controlled hydrolysis of the titanium-containing precursor (TIOT) in presence of nitric acid. The synthesis of mixed titanium silicon oxides has thus been made possible.

Clear evidence for a granular structure on the nanometer-scale has been found by transmission electron microscopy. Fig.7(a) shows a bright field image of a cross section of a nanocomposite $\text{Ti}_{0.5}\text{Si}_{0.5}\text{O}_2$ film. The film was deposited on a preoxidized silicon wafer. In bright field, the titanium-rich regions appear as dark grains. Fig.7(b) shows a dark-field image of the same region of the sample. Here, suitably oriented nanocrystals appear as bright spots. It can be assumed that the material consists of TiO_2 nanocrystals embedded in a matrix of amorphous silicon dioxide.

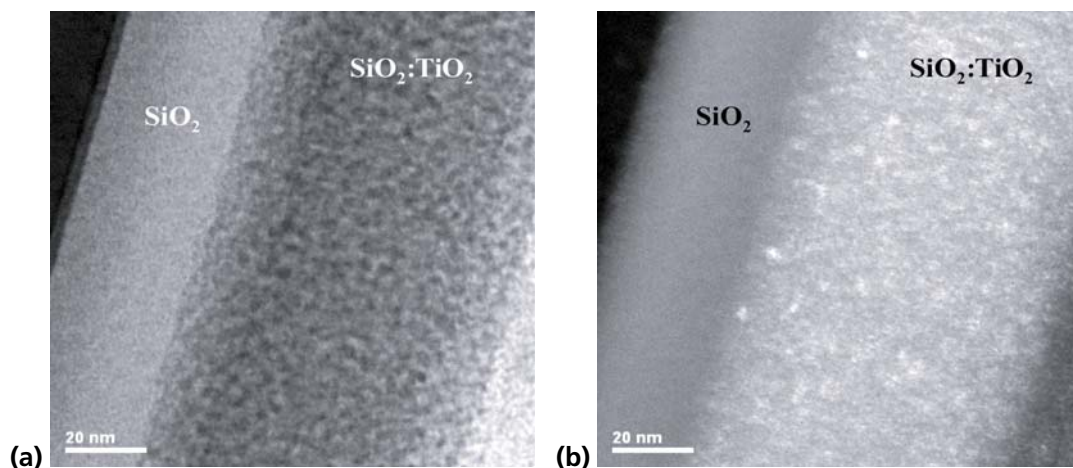


Fig.7: Transmission electron microscopy of a cross section of a nanocomposite $\text{Ti}_{0.5}\text{Si}_{0.5}\text{O}_2$ film.

(a) Bright field image: Ti - rich regions appear as dark grains

(b) Dark field image: TiO_2 nanocrystals with suitable orientation appear as bright spots

By adapting the stoichiometry, the refractive index of these nanocomposite $\text{Ti}_{1-x}\text{Si}_x\text{O}_2$ films can be effectively and continuously be controlled within a wide range, rendering this material very useful for the application in multilayer interference stacks. Fig.8 illustrates the dispersion relations

obtained from a series of samples with varying atomic concentration ratio of titanium and silicon. Most presumably these films consist of TiO_2 nanocrystals being imbedded in an amorphous SiO_2 matrix. These results open up manifold possibilities and considerable freedom in coating design.

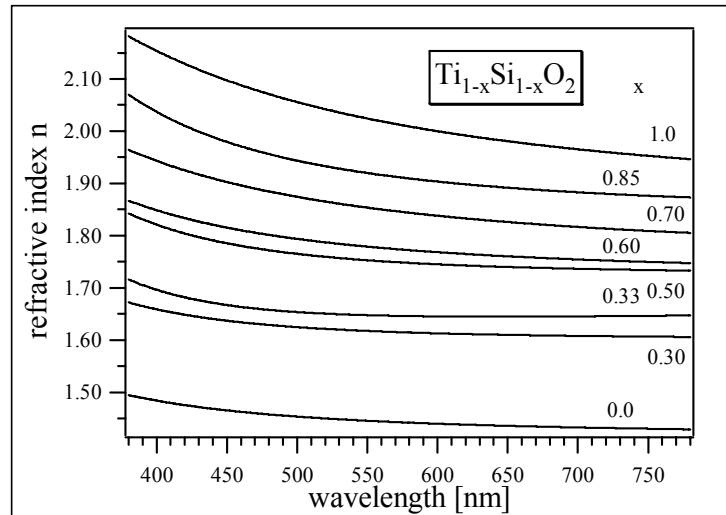


Fig.8: Dispersion relations $n(\lambda)$ for sol-gel deposited titanium silicon oxide films, as determined by spectrophotometry. Most presumably these films consist of TiO_2 nanocrystals being imbedded in an amorphous SiO_2 matrix.

3.2 Deposition of multilayers on A4 - sized substrates

By cycling dip-coating and thermal annealing, colored multilayers have been deposited on A4 - sized glass panes with a low iron content (thickness 4 mm, solar transmission 89.4%).

SiO_2 and $\text{Ti}_{0.3}\text{Si}_{0.7}\text{O}_2$ were chosen as low and high index materials, respectively, and the withdrawal speeds in the dip-coating process were adapted to yield the desired film thicknesses.

A cross-sectional TEM view of a multilayer stack is shown in Fig.9. In bright field, the nanocomposite $\text{Ti}_{0.5}\text{Si}_{0.5}\text{O}_2$ layers appear in dark grey, while the SiO_2 layers appear in light grey. In contrast to the homogeneous SiO_2 layers, the granular nanostructure of the $\text{Ti}_{0.5}\text{Si}_{0.5}\text{O}_2$ layers can clearly be distinguished.

Photographs of two colored samples (brownish and light blue) are shown in Fig.10. The homogeneity and quality of the coatings are satisfying. The solar transmittance of the blue sample is diminished by only 1.4 percent points with respect to the uncoated substrate, while the decrease in solar transmittance amounts acceptable 3.4 percent points for the brownish sample. The optical data yield a visible reflectance of 14 % and 12.6 % for the blue and brownish sample, respectively.

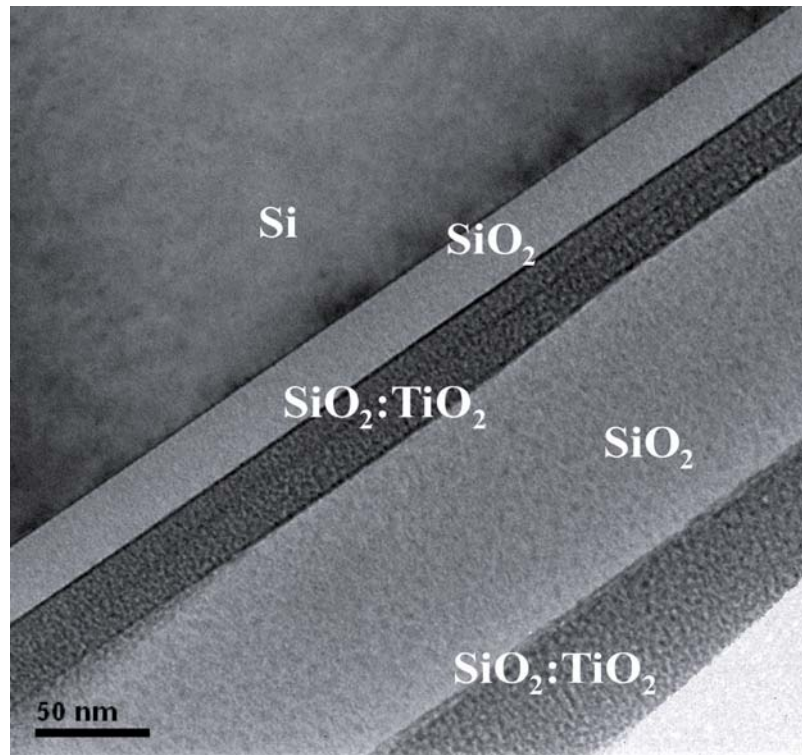


Fig.9: Transmission electron microscopy of a cross section of a $\text{Ti}_{0.5}\text{Si}_{0.5}\text{O}_2/\text{SiO}_2$ multilayer stack (bright field). The nanocomposite TiSiO_2 layers appear in dark grey, while the homogeneous SiO_2 layers appear in light grey.



Fig.10: Sol-gel deposition of nanocomposite oxide coatings on A4 - sized substrates.
(a) Photograph of glass panes coated with colored multilayer stacks. The loss in solar transmittance due to the colored coating amounts to only 1.4 percentage points (blue sample) and 3.4 percentage points (brownish sample). The optical data yield a visible reflectance of 14.0 % and 12.6 % for the blue and brownish sample, respectively.

4. Thin film materials with low refractive index (low-n materials)

Numerical calculations [4] showed that the use of refractive indices lower than that of silicon would favor a higher solar transmission at a given value of visible reflectance. Therefore not only the continuous control but also low values of the refractive index are desired. Among common sol-gel materials (mostly oxides, formed during annealing in air), silicon dioxide exhibits the lowest refractive index of approximately 1.47. Thin film materials with lower refractive index than that of SiO_2 are also useful for the application as anti-reflection coatings on glazing of solar thermal collectors and photovoltaics.

4.1 Porous silicon dioxide

One way to decrease the refractive index of silicon dioxide is to introduce voids into the coating structure. However, in vacuum deposition processes the formation of pores is difficult to control. By adding organic macromolecules to sol-gel precursor solutions, xerogel films can be created which contain nanometric organic regions. In the subsequent annealing step, the organic macromolecules can be oxidized, thereby leaving behind nanometric pores.

As a macromolecule, polyethylene glycol PEG was chosen and added to the precursor solutions. Highly transparent porous SiO_2 films have been produced during the tempering step. Fig.11 illustrates the evolution of normal transmittance spectra during pore formation (spectra as deposited and after one annealing step at 200°C, 350°C, 450°C and 550°C, respectively). After the heat treatment at 550°C the spectral transmittance at wavelengths around 550 nm surpasses 98.5%.

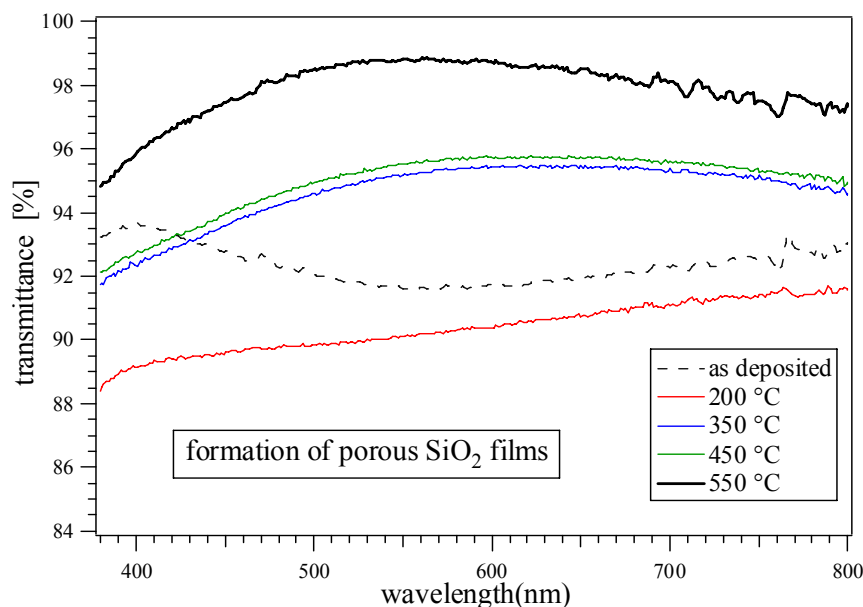


Fig.11: Evolution of normal transmittance spectra during pore formation (spectra as deposited and after one annealing step at 200°C, 350°C, 450°C and 550°C, respectively). After tempering at 550°C the spectral transmittance at wavelengths around 550nm surpasses 98.5%.

Ellipsometric data as measured from a nanoporous SiO_2 film deposited on a preoxidized silicon substrate are displayed in Fig.12(a). In the three-dimensional diagrams, the ellipsometric quantities $\tan(\psi)$ and $\cos(\delta)$ are plotted as a function of the wavelength and the angle of reflection. The analysis of these data is based on the fit of a Cauchy-type dispersion relation and yields the precise film thickness of the thermal silicon oxide (27 nm) and of the porous sol-gel film (152 nm), as well as the dispersion relation $n(\lambda)$ [see Fig.12(b)]. Using the Bruggeman effective medium theory, a pore volume fraction of 30 % is estimated from the low refractive index values (approximately 1.32 at 600 nm).

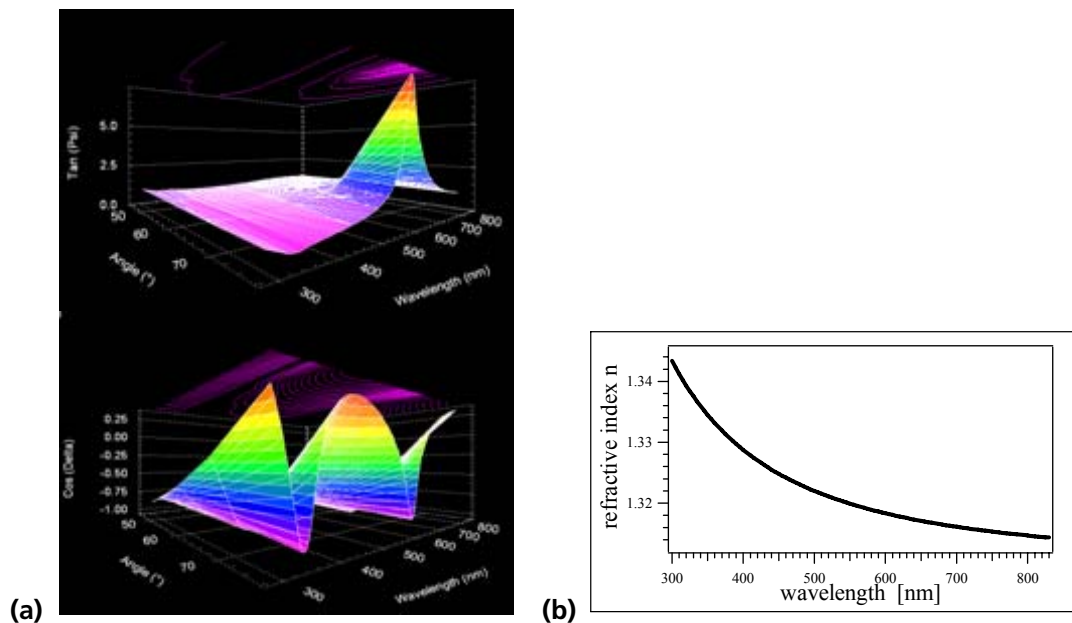


Fig.12: Ellipsometric determination of the refractive index $n(\lambda)$ of nanoporous silicon dioxide. (a) Measured data for the ellipsometric quantities $\tan(\psi)$ and $\cos(\delta)$. (b) Refractive index $n(\lambda)$, as inferred by the numerical analysis of the experimental data. A pore volume fraction of 30 % is estimated from the low refractive index values.

4.2 Magnesium fluoride (MgF_2)

The long-term optical performance of porous thin films might be degraded by hydrocarbons filling up the voids. An alternative approach to low-index materials is provided by fluorides such as MgF_2 , which are compact materials but in general softer than SiO_2 . In the annealing step following the deposition of the xerogel layers, the thin films are commonly exposed to air and thus hardening and oxidizing at the same time. Tempering in nitrogen atmosphere, which would preserve the fluorides from oxidizing, can be envisaged but would mean an additional cost-rising effort. A common precursor for the sol-gel synthesis of MgF_2 is hydrofluoric acid HF. Due to its extreme chemical violence (HF attacks even glass) its use should be avoided.

A much less violent precursor, trifluoroacetic acid (TFA) has been used for the production of pure magnesium fluoride films. The wettability of the used solutions appeared to be somewhat critical and not always satisfying. MgF_2 films have finally been obtained as well by annealing in nitrogen atmosphere as in ambient air. For the annealing in nitrogen, a special bakeout reactor was used, but it turned out that MgF_2 films could be formed as well by normal tempering in air. Fig.13 illustrates the dispersion relation $n(\lambda)$ of sol-gel deposited MgF_2 films. A dependence of the refractive index on the annealing temperature is observed, rising the question whether at 400°C a small volume fraction of pores is formed. Due to the observed wettability problems and haze formation during annealing, the quality of the deposited thin films is rather moderate as compared to the titanium silicon oxide films.

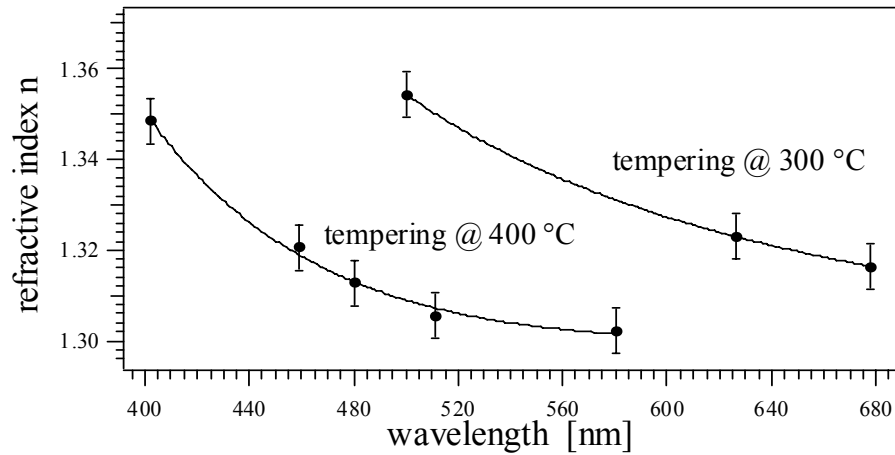


Fig.13: Dispersion relation $n(\lambda)$ of sol-gel deposited MgF_2 films. A dependence of the refractive index on the annealing temperature is observed, rising the question whether at 400°C a small volume fraction of pores is formed.

4.3 Novel fluoride/oxide nanocomposite thin films

Magnesium fluoride MgF_2 is one of the rare thin film materials exhibiting a refractive index lower than that of SiO_2 . Its application is restricted though by its lower hardness and eventually occurring adhesion problems. Magnesium fluoride might however be perfectly suited for lowering the refractive index of SiO_2 when introduced as nanometric aggregates. A nanocomposite material shall thus be created, based on the two constituents MgF_2 and SiO_2 .

Precursor solutions have been developed which are compatible with each other when mixing them after separate hydrolysis. Annealing can be performed simply in ambient air. Due to a better wettability, the dip-coating process turned out to be much less difficult than for the pure MgF_2 precursor solution. In addition, the tendency to haze formation is much lower, yielding a considerably higher film quality. The presence of magnesium and fluorine in the finally formed coatings has been confirmed by energy-dispersive X-ray microanalysis (EDX). Fig.14 shows the X-ray spectrum obtained from a likewise deposited thin film exhibiting the characteristic emission lines for the elements Si, O, Mg, and F (the line attributed to carbon is most presumably due to surface contamination by hydrocarbons).

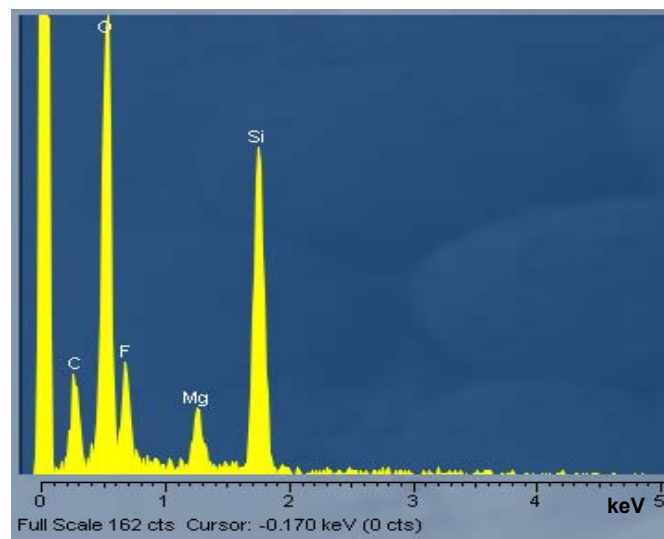


Fig.14: Energy-dispersive X-ray microanalysis of a quaternary thin film. The characteristic emission lines for the elements confirm the presence of Si, O, Mg, and F. The line attributed to carbon is most presumably due to surface contamination by hydrocarbons.

The film morphology is illustrated by Fig.15. The TEM images have been obtained from a cleaved corner of a Mg-F-Si-O film sandwiched between two SiO_2 layers. While in bright field the nanostructure is barely visible [Fig.15(a)], the dark field image shown in Fig.15(b) exhibits clearly bright spots in the region of the Mg-F-Si-O film. These features are a typical signature of a nanocomposite material. Further investigations will be necessary to clarify the exact nature of the nanostructure.

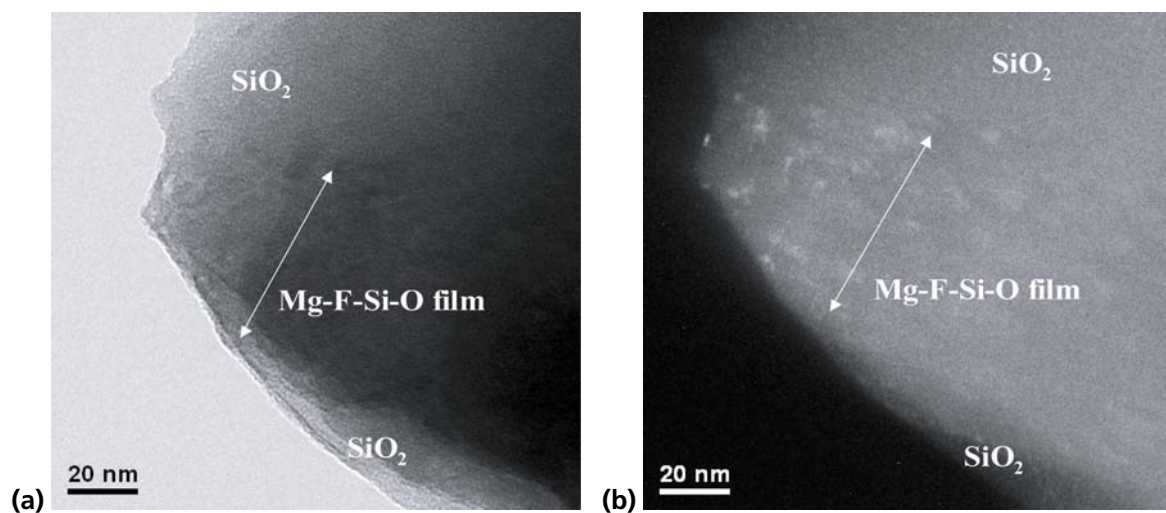


Fig.15: Transmission electron microscopy of a cleaved corner of a nanocomposite Mg-F-Si-O film sandwiched between two SiO_2 layers.

(a) Bright field image: the nanostructure is barely visible

(b) Dark field image: the bright spots are a typical signature of a nanocomposite material

Fig. 16(a) shows ellipsometric data as measured from a Mg-F-Si-O//SiO₂ tandem layer deposited by two sol-gel dip-coating cycles on a silicon substrate. The numerical analysis of the $\tan(\psi)$ and $\cos(\delta)$ spectra yields film thicknesses of 138 nm and 130 nm for the SiO₂ and Mg-F-Si-O layers, respectively.

Remarkably low refractive index values are found [see Fig.16(b)]. The observed range from 1.255 to 1.270 is extremely interesting for single-layered anti-reflection coatings on solar collector glazing, as well as for multilayered colored coatings with a high solar transmission.

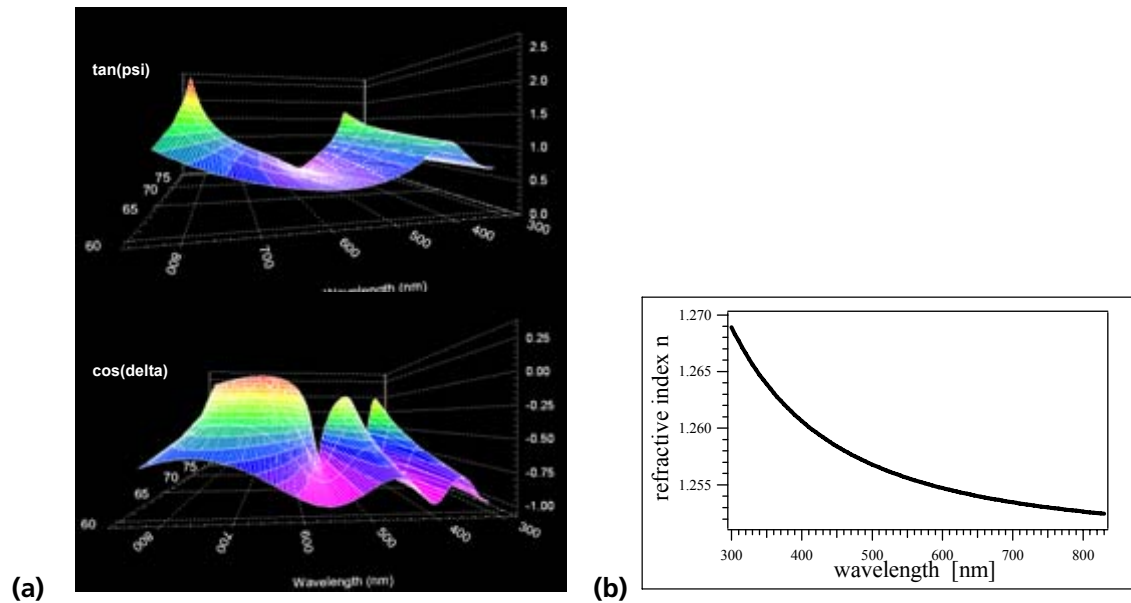


Fig.16: Ellipsometric determination of the refractive index $n(\lambda)$ of nanocomposite Mg-F-Si-O films.

(a) Measured data for the ellipsometric quantities $\tan(\psi)$ and $\cos(\delta)$

(b) Refractive index $n(\lambda)$, as inferred by the numerical analysis of the experimental data. Remarkably low refractive index values are found.

Measurements of normal spectral transmittance on a large set of samples have shown broad spectral maxima exceeding 99.5 % for Mg:Si molar ratio ranging from 30:70 to 60:40. In Fig.17, transmittance spectra of thin films on glass are shown for varying film thickness (Mg:Si molar ratio 50:50).

The total solar T_{sol} transmission for the 114 nm thick sample, exhibiting a maximum of 99.8 % centered at 571 nm, has been measured for $\lambda = 250$ to 2500 and compared to the uncoated glass substrate (see figure 18). A large increase in T_{sol} is observed for the nanocomposite coated sample: a total amount of 97.2 % is reached while the uncoated substrate exhibits a solar transmission of 91.7 %.

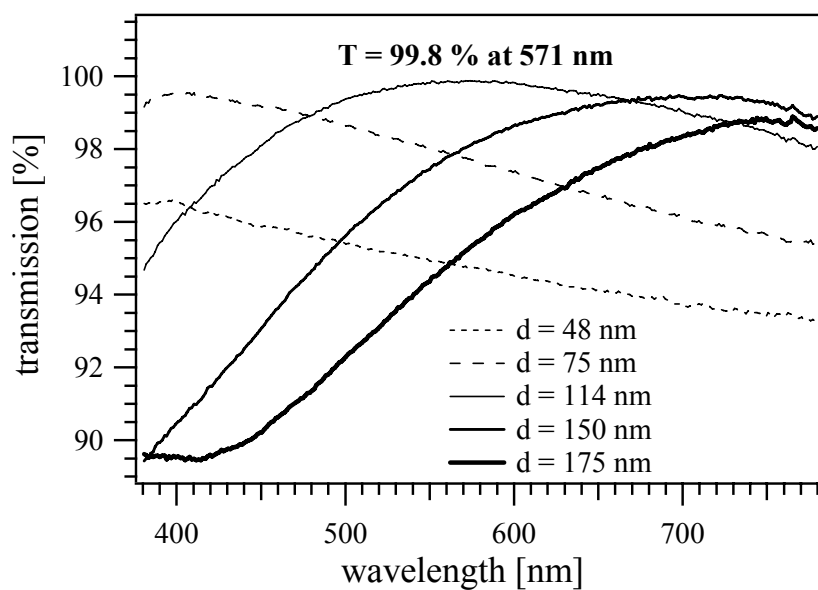


Fig.17: Transmittance spectra of Mg-F-Si-O thin films on glass (Mg:Si molar ratio 50:50). The thickness had been varied from $d = 48$ to 175 nm, by adapting the withdrawal speed. A maximum of 99.8% is reached for the spectral transmittance of the 114 nm thick sample.

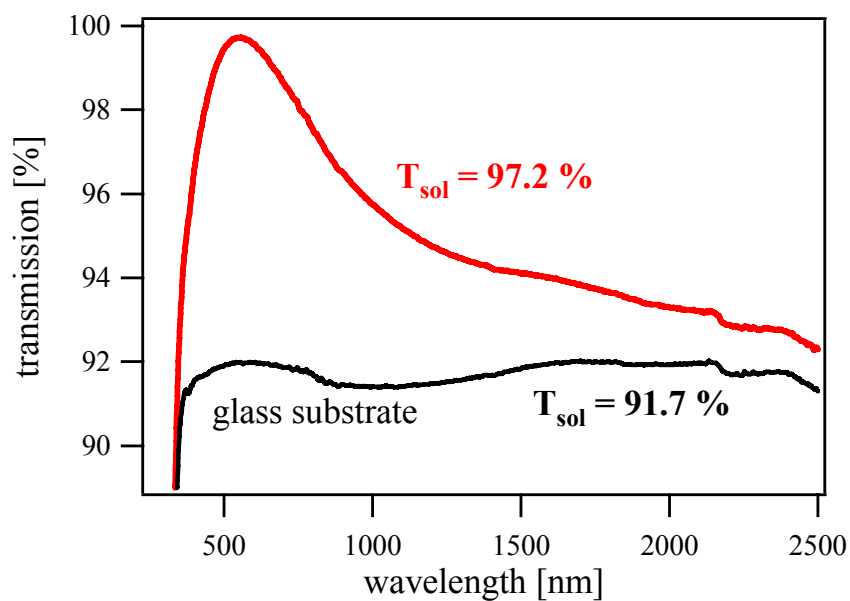


Fig.18: Total spectral transmittance of a 114 nm thick Mg-F-Si-O thin film on glass (Mg:Si molar ratio 50:50). The antireflective effect raises T_{sol} from 91.7% to 97.2% . For comparison, the transmittance spectrum of an uncoated substrate has been added to the diagram.

5. Film hardening by UV-curing

For the industrial production of multilayers by the sol-gel process, UV-curing shall replace the thermal annealing step needed after the deposition of each individual layer. Film hardening by UV exposure will result in speeding up the process and saving energy, thereby reducing costs significantly.

5.1 UV radiation source

A special UVC radiation source has been designed and built. Two UVC discharge tubes are mounted in a suitable housing in order to irradiate the substrate from both sides [Fig.19(a)]. The electrical power of each tube emitting at a wavelength of 254 nm amounts to 15W, the irradiation in the vicinity of the entrance slit is in the order of 8 mW/cm^2 . The source is attached to the dip-coater, which guarantees a continuous displacement of the substrate [Fig.19(b)]. The assembly is placed into the laminar flux chapel [for a photograph see Fig.19(c)], which has been thoroughly equipped with UV-absorbing panes and a safety interlock. Outside the likewise screened chapel, the level of UVC radiation is below the detection threshold of the UV-radiometer ($4 \mu\text{W/cm}^2$).

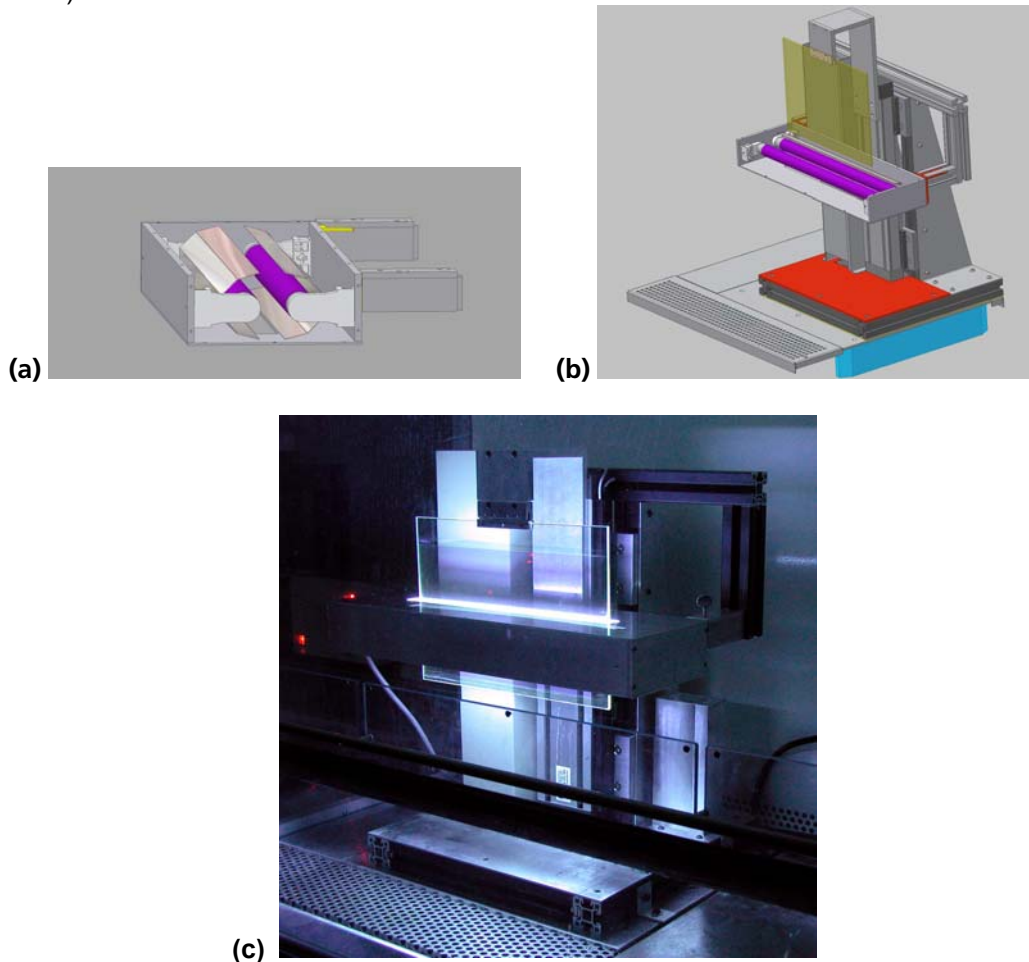


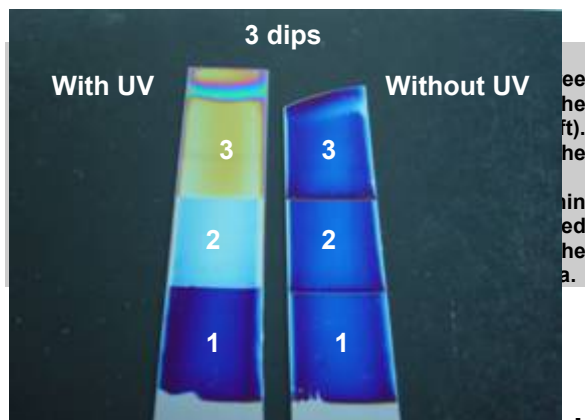
Fig.19: Set-up for film hardening by UV-curing
 (a) Schematic drawing of the UVC radiation source (principal emission wavelength 254 nm)
 (b) The source is attached to the dip-coater which guarantees a continuous displacement of the substrate
 (c) Photograph of the dip-coater equipped with the UVC radiation source. The assembly is placed in a laminar flux chapel which has been equipped with UV-screens.

5.2 Photosensitization of the used precursor solutions

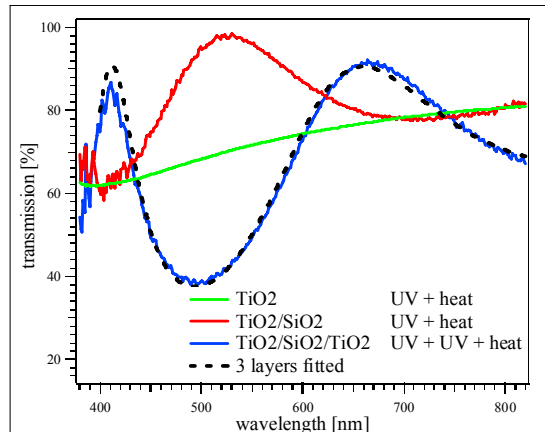
By introducing a photoinitiator, a UV-induced photopolymerization can be achieved, allowing the likewise hardened Xerogel film to be resistant towards dissolution in the next precursor solution.

UV-polymerizable silicon and titanium oxide solutions have been developed by the introduction of functional groups attached to the precursor molecules and by the addition of a photoinitiator in order to start the reaction. Methacrylic acid ($C_4H_6O_2$) combined with metal alkoxides has proven to form reactive groups after several thermal treatment and concentration steps. Irgacure 184 provided by CIBA was chosen as photoinitiator.

Multilayers of TiO_2 , SiO_2 and $Ti_{0.5}Si_{0.5}O_2$ were prepared by deposition of successive layers with intermediate exposure to UV radiations (total energy higher than 2 J/cm^2). A final annealing step was maintained to transform the organic xerogel films in the appropriate oxide compounds. Comparison with multilayered samples deposited without UV-exposure has clearly demonstrated the stabilizing effects of the UV-curing steps. Non-irradiated xerogel films exhibit dissolution during second and third dipping in the solutions, resulting in single-layer coatings [see Fig.20(a)]. Classically annealed multilayers have been prepared in parallel and compared by spectral transmission and ellipsometric measurements to the UV-cured samples. Only negligible differences have been observed either in the optical properties or in the structure of the coatings. UV-polymerization of xerogel films has been applied to the realization of colored coatings by deposition of TiO_2 and SiO_2 layers alternatively. High quality samples have been obtained with expected optical properties [see Fig.20(b)].



6. Demonstration of sol-gel deposited samples (substrate size A4)



In order to provide a convincing demonstration for architects and industry, a collector model ("Demo-Box") was built, which can be used to expose the A4 sized colored glazing samples with a real selective black absorber sheet behind. The colored glass panes can be combined with differently textured front glazing in order to study the effect of diffusing surfaces/interfaces. This Demo-Box has proven to be very helpful in order to demonstrate the feasibility of the original idea and to visualize the design possibilities for colored solar facades.

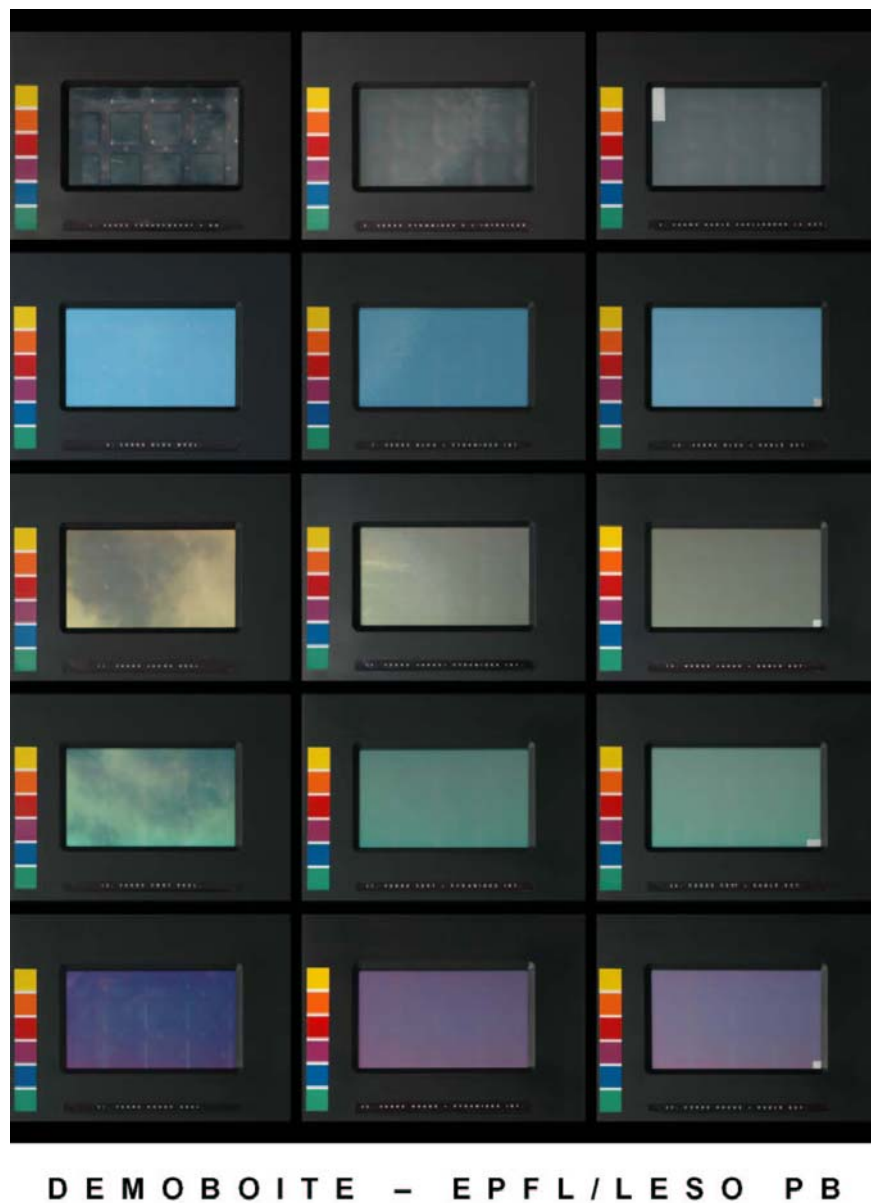


Fig.21: Demonstration of sol-gel deposited coatings on A4 - sized glass panes. Various color shades are combined with different surface textures and a black selective absorber sheet behind the glazing. Top left: untreated solar glass for comparison.

7. Prototype fabrication of colored collector glazing on the industrial scale by magnetron sputtering (substrate size 1.90 m x 3 m)

Prototypes of colored glazing on large panes of solar glass (dimensions 1.90 m x 3 m) have been prepared by magnetron sputtering with the collaboration of the company GLAS TRÖSCH, Switzerland. The possibilities and boundary conditions of the existing equipment have been discussed with Fabian Zwick, GLAS TRÖSCH. Computer simulations of the envisaged multilayer designs have been performed at EPFL-LESO using refractive index data on sputtered films. After optimization, promising combinations of thin film materials and film thicknesses have been identified within respecting the boundary conditions given by the existing equipment. Glass panels have been realized in different color shades (light blue, green and yellow).

A light blue glazing was cut to measure and for the first time installed on a real-sized solar collector (AZUR20, AGENA, dimensions 0.93 m x 2.43 m). The result fulfilled completely our aesthetical requirements. The colored glazing is hiding the absorber, and the color of the coating is rather stable with respect to a variation of the viewing angle.



Fig.22: AGENA solar collectors covered equipped with a conventional collector glazing (on the left) and with the novel blue-colored coated solar glazing (on the right).

In order to achieve a mat appearance, an etching treatment has been applied to the non-coated surface of some of the colored glass panes. The resulting rough surface diffuses the transmitted and reflected light, and contributes to hide the absorber. The etching process was provided by the Swiss company FALLÄNDER GLAS AG. During the latter treatment, a patterning of the front surface can be achieved on demand.

Large scale collector prototypes have been fabricated by mounting likewise treated panes on solar collectors from SCHWEIZER (dimensions 1.20 m x 2.10 m). The aesthetically very pleasing collectors have been exposed at EPFL-LESO (see Fig.23). Different color choices are illustrated by Fig.24.



Fig.23: Solar collectors from SCHWEIZER covered with light blue glazing. An etching treatment has been applied on the outer side of the glass. The etched surface can be patterned on demand, giving a large freedom in design possibilities.



Fig.24: Light blue, green and yellow glazing (dimensions A4) presenting a choice of diffusing and textured surface treatments, offering at the same time a smart way to customize their appearance. The absorbers are perfectly hidden, and the eye is attracted to the plane of the glazing.

8. Architectural integration of the novel colored solar collectors

The architectural integration activities in this project were concentrated on three goals:

- Study and optimize the various glass treatments from the architectural point of view (colors, acid etching, patterns etc...)
- Explore the necessary architectural conditions needed to fully exploit the new glazing, with dimensional flexibility, material appearance and jointing being key issues. Explore the possibilities opened by the use of the same glass for collectors and insulation cladding
- Prepare demonstration material, publications and presentations to spread the idea and collect feedback from potential users.

8.1 Glass treatments.

To reach the desired level of masking effect of absorber and piping, the selective filter is not sufficient in all lighting conditions: as the base of the masking effect is the light reflected from the filter, if the incoming light is not reflected in the direction of the observer, there is no or very limited masking. With the specularity of standard untreated glass this can happen quite often. To overcome this problem, a diffusing treatment can be applied on the outer side of the glass, distributing the light reflected by the filter in all directions and achieving the masking. Several options are open, from structured glass to various ways of altering the glass surface (acid etching, sand projection...).

Using the Demobox, designed to simulate a mini solar collector with real absorber parts inside (Energie Solaire), we tested several diffusing options in combination with A4 filter samples produced at LESO.

The “Pyramids” structured glass as well as acid etching, sand and stone projections were amongst the most promising possibilities.

Using parts of the first large scale prototype glasses coated by Glas Trösch by magnetron sputtering, we have been able to test on A4 format samples the various diffusing treatments on industrially coated glass. Several sub-options were also tested like acid etched regular patterns and even custom designed etchings (text, logo etc...) to demonstrate the new freedom level to users.

These samples allowed us to select the treatments of the two first large scale glasses cut to Schweizer collector size: Fällander H16 acid etching standard and Fällander H16 with small squares pattern (Fig.27)

8.2 Architectural integration

As shown by a large European survey conducted within the project SOLABS, colored collectors can ease the work of the architect but are not **the** answer to all integration problems. An important work on the ideal flexibility level that collectors should offer to be best integrated into facades has been conducted. The analysis of the detailed survey results highlighted how all the system characteristics affecting the building appearance have an impact on integration quality. They can be summarized as follows:

- Size and position of collector field
- Shape and size of the modules
- Type of jointing
- Collector material and surface texture
- Absorber colour

For a successful integration all these characteristics of the solar system have to be coherent with the global building design logic.

We also completed a Swiss market survey on the flexibility of present collectors that shows the poor flexibility of most products according to these characteristics (Table 1).

Solar thermal systems manufacturer	Flat plate collectors systems										Evacuated tubes systems	
	Glazed									Unglazed		
	1.a	2.a	3.a	4.a	5.a	6.a	7.a	8.a	9.a	1.b	1.c	2.c
m2 produced in 2006	70'000	12'000	4'000	3'000	2'350	1'000	600	350	-	2'516	21'000	1'200
part installed in CH	12%	98%	100%	98%	99%	90%	100%	100%	-	40.4%	2%	55%
m2 installed in CH	8'400	11'760	4'000	2'940	2'320	900	600	350	-	1'016	420	660
Swiss Market part	17%	24%	8%	6%	5%	2%	1.2%	0.7%	-	100%	28%	44%
own mounted	2.2%	7%	50%	5%	2%	50%	100%	100%	-	41.2%	0.1%	20%
façade applications	0%	3%	4%	0%	0%	2%	10%	0%	-	23%	0.5%	20%
Facade products	-	-	-	-	-	- (1)	+	-	-	-	-	+
Availability of dummies	-	-	-	-	-	-	+/(3)	-	-	+	-	-
shape& size flexibility	-	+	-	-	-	+/-	+	+/-	-	+	-	+
glazing surface texture choice	-	+	-	-	-	+/-	+/-	-	-		-	-
absorber surface texture choice	-	+/-	-	-	-	-	-	-	-	-	-	-
absorber colour choice	-	+/(4)	-	-	-	-	-	-	-	-	-	-
jointing options	-	-	-	-	-	-(1)	+/-	-	-	-	-	+

Table 1: (1) producer 6.a is at present developing a novel collector module for facade use, characterized by easy facade fixing system and aluminium framed jointing. (2) Façade products are proposed in terms of solar shading and balcony parapets. (3) Dummies can be produced on specific demand (4) Three collectors colours are available (black, blue and bronze)

Looking at our glazing from the point of view of flexibility, it becomes clear that it has much more to offer than simply hiding the absorber.

As this new glazing can also be used as simple cladding over insulation, it allows the architect to use the same glass over all non transparent parts of his facades and to implement exactly the needed amount of collectors, regardless of the façade area distribution. This answers to the “Size and position of the collector field” requirement. It equally well answers to “Collector material and surface texture” and “Absorber colour” freedom levels. The last two points “Shape and size of the modules” and specially “Type of jointing” have still to be worked on but can certainly be satisfied with some efforts.

Combining all the characteristics needed to design an **active façade system**, this glazing should allow us to propose new solutions. In several publications, we give recommendations on the respective roles of collector producers and façade manufacturers in this new market, according to their specific fields of expertise.

Photoshop simulations of such systems were proposed to support this idea (example given at Fig.25).



Fig.25: LESO glazing integration simulation over Pully school (CH) Active and non active areas.

8.3 Demonstration material, publications and contacts.

To control the effects of the various treatments and test several options at a scale architects could work with, we developed the already mentioned fake mini collector DemoBox. This was extensively used for the planned research and development activities first and then as demonstration tool for external use.

As the number of interesting samples grew rapidly, the need for a simultaneous comparison between options appeared, leading to the development of three DemoStrips, hosting 4 glasses (Fig.26).

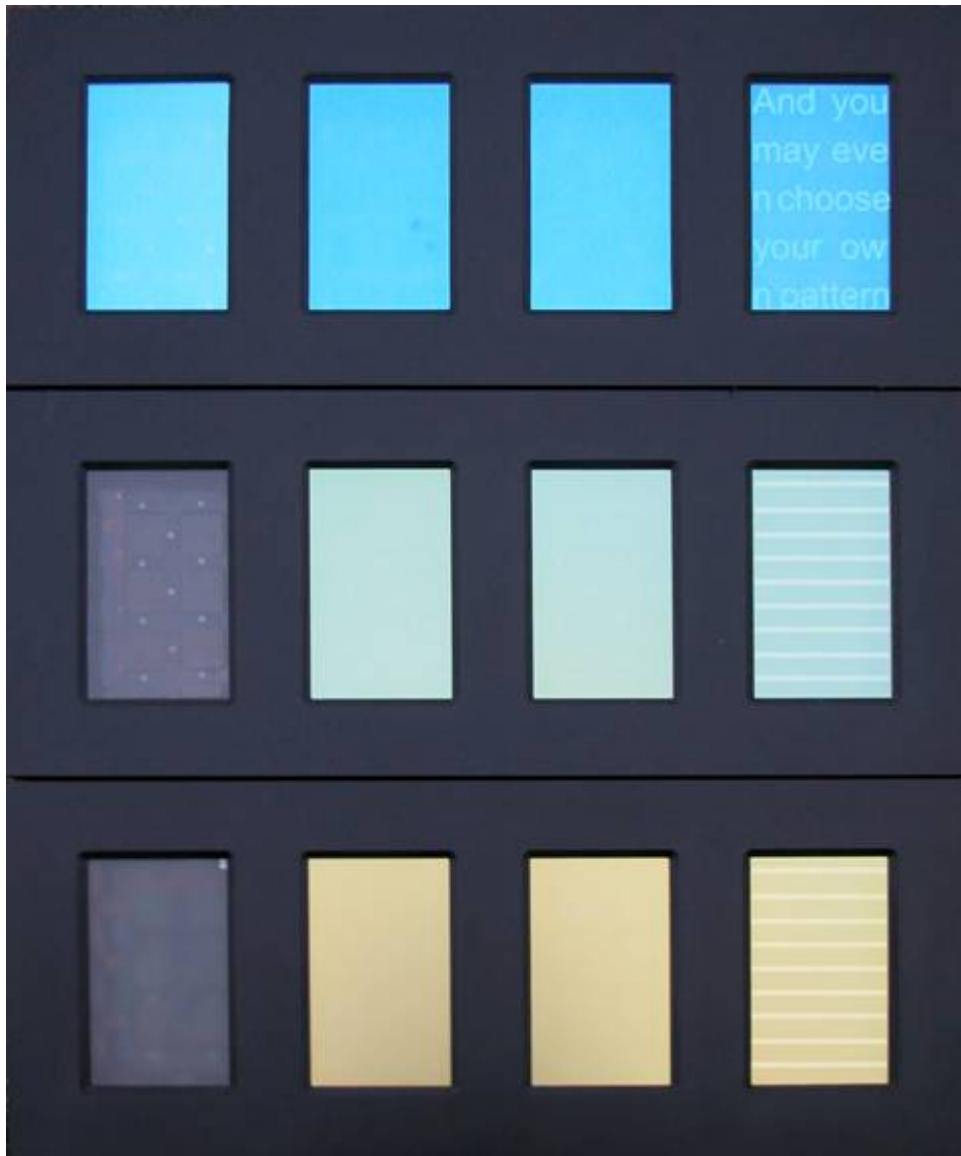


Fig.26: The three DemoStrips with various colours and patterns

They have been used on one hand to explain quickly the principle of the glazing (for example: extra white glass, frosted white glass, filter alone, filter and diffusing treatment) and to compare simultaneously various colors and/or various diffusing treatments

Contact has been made with the company Schweizer Metallbau, active in both solar collectors and façade markets. They were convinced enough to donate three real size collectors with the major advantage of having only the EPDM joint holding the glass. This allowed us to easily try our new large size glasses on their collector without any change or adaptation.

Fig.27 shows on the left the naked absorber and on the right the same collector with the new glazing.

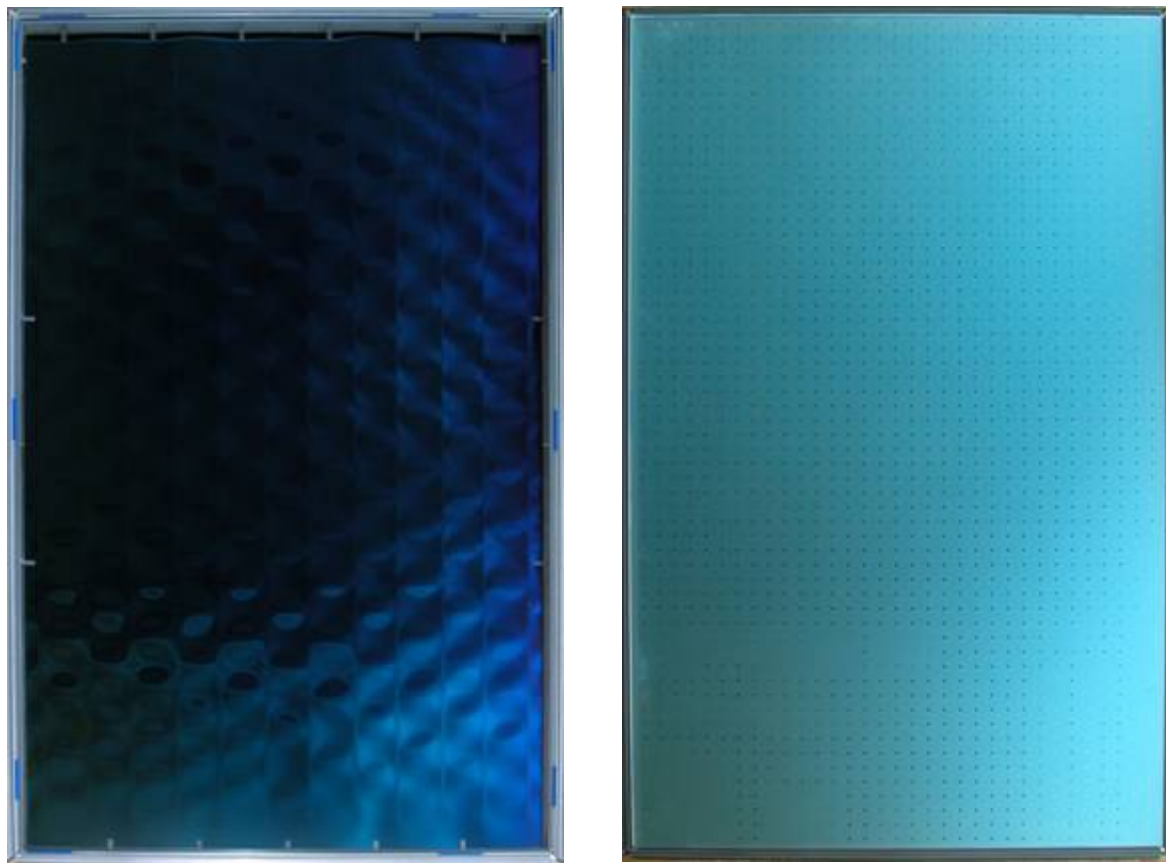


Fig. 27: naked absorber and the same collector with the new glazing.

We could also show the collector with our glass at Energissima and CISBAT, getting a very positive feedback from professional and amateurs alike.

To get a more detailed feed back from the future players needed to successfully introduce the new glazing, we visited practicing architects and collector manufacturers interested in façade integration both in Switzerland and Austria. Amongst the visited companies are AKS Doma and Winkler in Austria, Agena, Schweizer Metallbau, Soltop etc... in Switzerland.

The results of the project, considered from the architectural integration point of view, have been presented to several international Conferences (ISES, PLEA and CISBAT), at IEA Task 39 meetings and to a new INTERREG project preparation meeting.

Fig.28 shows Schweizer collectors equipped with two new glazing exhibited at the LESO, with the development team in front.



Fig. 28: Demonstration collectors and project team.

Industry contacts

- Presentation of a model collector with the dimensions 20 cm x 30 cm (the “Demo-Box”) to possible industrial partners (AGENA, CLIPSOL, SCHWEIZER, AKS Doma, Winkler...) and to architects (Hestness, Rejenka, Müller, Kempfen...)
- Collaboration with GLAS TRÖSCH and FÄLLANDER GLAS on the prototype production of the novel collector glazing
- Discussions with CENTROSOLAR GLAS GmbH, Germany (former FLABEG) concerning the prototype fabrication of the novel collector glazing by sol-gel dip-coating
- ASULAB (SWATCH GROUP) donated equipment for vacuum deposition of thin films, suitable for multilayer deposition of colored coatings on solar collector glazing
- A new CTI project on sol-gel deposition of nanostructured selective solar absorber coatings is in preparation. Industrial partner: the Swiss solar collector manufacturer ENERGIE SOLAIRE SA
- Discussion with H+S Solar for a possible collaboration

National Collaboration

A close collaboration exists with the research group of Prof. Peter Oelhafen, Institute of Physics, University of Basel. Jamila Boudaden provided the refractive index data of sputtered oxides for the simulation of the prototype coatings. The collaboration can be characterized as cooperative and productive.

Within EPFL, the project benefits from the accessibility to electron microscopes and to the facilities of TEM sample preparation at the Interdepartmental Center of Electron Microscopy CIME. Especially mentioned should be the excellent technical and scientific support by Guido Milanesi, Danièle Laub, Dr. Aïcha Hessler, Dr. Marco Cantoni, Fabienne Bobard, and Prof. Philippe-André Buffat.

The research group of Prof. Libero Zuppiroli (LOMM at EPFL) offered us access to their new ellipsometer. We appreciate especially the spirit of scientific collaboration in this group and the discussions with the collaborators Michel Schär, Dr. Rolando Ferrini, and Dr. Olivier Nicolet.

The results of the project will be used within a national CCEM-CH project "Innovative Building Technologies for the 2000-Watt Society (House2000)"

International Collaboration

- European project **SOLABS**,

Partners from France, Spain, Slovenia, Germany and Switzerland. Even though the topics of glazed and unglazed thermal solar collectors are clearly separated, synergies emerge especially regarding architectural aspects.

Name of Project:

"Development of unglazed solar absorbers (resorting to coloured selective coatings in steel material) for building facades, and integration into heating systems"

EU project number: NNE5-2001-00963

- Collaboration with Polymer Competence Centre **PCCL**, University of Leoben, Austria,

Theory and modelling of thin film optics, group Dr. Dieter Gruber

- **Invited keynote lecture at the ESF exploratory workshop** on carbon based nanostructured thin films in Gdansk, Poland, with participants from Austria, Belgium, the Czech Republic, France, Germany, Greece, Italy, Lithuania, Poland, Portugal, the Slovak Republic, Slovenia, Sweden, Switzerland, and Turkey.

A new European network on nanostructured thin films is envisaged by the workshop participants.

A.S. is main organizer of the symposium on carbon based nanostructured thin films for the 2008 spring meeting of the European Materials Research Society E-MRS

Evaluation and Outlook

Achievements made in 2006 concern various aspects of the project: the nanostructure of the deposited thin films is directly imaged by transmission electron microscopy, the refractive index of advanced low n materials is measured accurately by ellipsometry, nanostructured films are deposited on the intermediate size scale (A4), the equipment for film hardening by UV curing has been built, first tests of the prototype fabrication on the industrial scale have been performed, and work on the architectural integration has been started.

All project goals have been accomplished:

1. Infrastructure for sol-gel deposition of multilayers on A4 - sized substrates (size A4)

An infrastructure for the handling of A4 sized samples has been established regarding substrate cleaning, multiple dip-coating and dust protected thermal annealing. All aspects of the cyclic process for multilayer deposition have been optimized yielding homogenous coatings free of visible defects.

2. Methodology of optical measurements

For the determination of the optical constants of the thin films, for the quantification of colors of reflection, and for the measurement of the solar transmittance of non-diffusing samples, well-working procedures based on spectrophotometry, ellipsometry, colorimetry, and on the use of a solar simulator have been established and validated.

3. Sol-gel deposition of nanostructured titanium silicon oxide films ($\text{Ti}_{1-x}\text{Si}_x\text{O}_2$)

Precursor solutions suitable for the deposition of such nanocomposite $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ thin films have been developed. The refractive indices of such nanocomposite films can be tuned continuously within a large range, giving large freedom for the design of multilayered interference filters. Multilayered coatings with a high energy efficiency of the colored reflection have been designed and prepared by cyclic sol-gel dip-coating.

4. Thin film materials with low refractive index (low- n materials)

The availability of thin film materials with a refractive index lower than that of silicon dioxide favors a higher solar transmission at a given value of visible reflectance.

The feasibility of the sol-gel deposition of the following materials has been demonstrated:

- porous SiO_2
- MgF_2
- novel fluoride/oxide nanocomposite thin films (quaternary Mg-F-Si-O films)

The optical constants of those materials have been determined precisely by spectrophotometry and spectroscopic ellipsometry. Their low refractive index makes them very interesting for coatings on solar collector glazing, as well anti-reflection coatings as colored coatings with high solar transmittance. Especially the novel fluoride/oxide nanocomposite thin films (quaternary Mg-F-Si-O films) are promising candidates for durable low-n coatings.

5. Film hardening by UV-curing

For the industrial production of multilayers by the sol-gel process, UV-curing can replace the thermal annealing step needed after the deposition of each individual layer. Film hardening by UV exposure will result in speeding up the process and saving energy, thereby reducing costs significantly.

The experimental infrastructure for UV-curing has been established (construction of a suitable UV source and installation of UV screening panels). The used precursor solutions have been modified in order to achieve a photosensitization yielding film hardening by photopolymerization. The fabrication of multilayers using intermediate UV-curing steps and one final thermal annealing procedure has been demonstrated in the laboratory.

6. Demonstration of sol-gel deposited samples (substrate size A4)

A model collector for a convincing demonstration of the A4-sized sol-gel samples was build and presented to architects, facade manufacturers and glass industry.

7. Prototype fabrication of colored collector glazing on the industrial scale by magnetron sputtering (substrate size 1.90 m x 3 m)

An industrial partner for the prototype fabrication of colored collector glazing has been found. The possibilities and limitations of eventually existing production lines were discussed, and adapted multilayer designs were be proposed according to the given boundary conditions. Real scale glass panes have been coated with the novel multilayers, and the novel glazing has been integrated into first prototype collectors.

8. Architectural integration of the novel colored solar collectors

The potential of the new glazing to ease façade integration of solar thermal has been demonstrated. Several diffusing glass treatments have been tested and proved valid solutions. The added flexibility in integration offered by the new glazing will allow the design of active facades, using the same glass for insulation cladding and collector cover.

Outlook:

Following the successes of this stage, we are clearly willing to further develop the glazing and its application.

On the glazing itself, the following points need further work:

- Filter optimisation for magnetron sputtering to minimize the transmission losses and select the colour
- Coating of industrial diffusing white glass, to lower the costs
- Tempering the coated diffusing glass for façade application
- Establish an industrial production scheme with price evaluation

On the architectural integration, we still need to:

- Test the glazing behaviour and optical characteristics in various environments (behaviour with joints, rain, by night etc..)
- Study the required conditions for the elements behind the glass that would ensure the masking effect (insulation, corner etc...)
- Adapt “incognito” collectors to be used directly by architects.
- Develop an active façade system in collaboration with a façade manufacturer

Proposal for a follow-up will be submitted beginning of 2008.

A parallel research of potential partner for a CTI/KTI project will be conducted.

Part of the result will be used in the project CCEM-CH House 2000

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Invited talks

A. Schüler, ***Thin films for thermal solar collectors***, invited seminar talk, November 2004, Institut für Solare Forschung Hameln ISFH, Germany

A. Schüler, ***Electronical and optical properties of advanced nanostructured materials a-Si_{1-x}C_x:H/Me***, From Solid State to Biophysics II, June 2004, Cavtat, Croatia

A. Schüler, ***Quantum dots in photovoltaic solar energy conversion***, From Solid State to Biophysics III, June 2006, Cavtat, Croatia

A. Schüler, ***Optical properties of metal-doped carbon-based nanocomposite thin films, invited keynote lecture***, ESF workshop on Carbon-Based Nanostructured Composite Films, September 2006, Gdansk, Poland

A. Schüler, ***Nanostructured Materials in Solar Energy Conversion***, Seminar of Condensed Matter Physics, October 2007, Institute of Physics, University of Basel

Further oral presentations

A. Schüler, ***Advanced nanostructured materials a-Si_{1-x}C_x:H/Me for the photothermal conversion of solar energy***, May 2004, SCELL2004, Badajoz, Spain

D. Dutta, ***Fabrication of multilayered thin film interference filters based on dielectric oxides prepared by the sol-gel method for a colored glazed thermal solar collector***, September 2004, Physics Department, Indian Institute of Technology IIT New Delhi, India

J. Chaney, ***Cracking the golden sample***, July 2004, EPFL, Lausanne

J. Boudaden, ***Dielectric interference layers for solar thermal collectors***, June 2004, EUROSUN 2004, Freiburg im Breisgau, Germany

A. Schüler, ***Angle-dependent spectrophotometry of sol-gel deposited multilayered oxide coatings on solar collector glasses***, CISBAT 2005 International Conference, Lausanne, 28-29 September 2005

M. Python, ***Photoluminescence of quantum dots for solar energy applications***, CISBAT 2005 International Conference, Lausanne, 28-29 September 2005

M.-C. Munari Probst, ***Integration and formal development of solar thermal collectors***, PLEA conference, 497-502, Beirut, 13-16 Nov. 2005

C. Roecker, A. Schüler, ***New developments for facade integration of solar collectors***, Assemblée annuelle des facadiers suisses, La Sarraz, déc 2005

E. De Chambrier, ***Nanostructured low refractive index materials on solar collector glazing***, EUROSUN 2006, June 2006, Glasgow, UK

C. Roecker, M.-C. Munari Probst, ***Capteurs solaires colorés et intégration architecturale***, October 2006, symposium ER 06, Yverdon

O. Bouvard, ***Couches minces sélectives pour capteurs solaires thermiques***, June 2006, Université Montpellier II, Institut Universitaire Technologique de Nîmes, France

C. Galande, ***Synthesis of photoluminescent nanocomposite thin films for solar collectors***, September 2006, IIT Kanpur, India

A. Kostro, ***PhotonSim - Développement d'un outil pour la simulation de concentrateurs solaires par tracé de rayons selon la méthode de Monte-Carlo***, July 2006, EPFL, Lausanne

M. Valle del Olmo, ***Characterization of external quantum yield and lateral energy losses in photoluminescent Quantum Dot solar concentrators***, July 2006, EPFL, Lausanne

R. Kukreja, ***Deposition and optical characterisation of thermochromic thin films based on vanadium oxide***, Metallurgical and Material Science Department, IIT Bombay, Mumbai, India

MC. Munari Probst, ***Façade Integration of Solar Thermal Collectors: Present and Future***, CISBAT 2007 International Conference, Lausanne, 4-5 September 2007

E. de Chambrier, ***Nanostructured coatings on glazing for active solar facades***, CISBAT 2007 International Conference, Lausanne, 4-5 September 2007

A. Schüler, ***Principles of Monte-Carlo ray-tracing simulations of quantum dot solar concentrators***, ISES solar world congress 2007, Beijing, China 18th-21st September 2007

A. Kostro, ***PhotonSim: developing and testing a Monte-Carlo ray-tracing software for the simulation of planar luminescent solar concentrators***, CISBAT 2007 International Conference, Lausanne 4th - 5th September 2007

Christian Roecker, ***Façade integration of solar thermal collectors: a breakthrough***, ISES solar world congress 2007, Beijing, China 18th - 21st September 2007

MC. Munari Probst, ***From Thermal Collectors Integration to Active Façade Systems***, PLEA Conference 2007, Singapore, 22nd - 25th November 2007

Poster Presentations

Schüler A., ***Designing thin film multilayers for colored glazed thermal collectors***, June 2004, EUROSUN 2004, Freiburg im Breisgau, Germany

Munari Probst M.-C., ***Impact of new developments of the integration into facades of solar thermal collectors***, June 2004, EUROSUN 2004, Freiburg im Breisgau, Germany

E. de Chambrier, ***Sol-gel deposition and characterization of low refractive index nanocomposite Mg-F-Si-O thin films for solar and protective coatings***, E-MRS Spring Meeting 2007, Strasbourg, May 28 – June 1, 2007

PhD work in progress

Estelle de Chambrier, tentative title of PhD thesis : ***Matériaux diélectriques nanostructurés pour vitrages colorés sur capteurs solaires thermiques***

Munari Probst M.-C, tentative title of PhD thesis : ***Solar thermal into facades: principles of architectural integration, and systems design methodology.***

Master's theses (related topics)

Andre Kostro, ***Photonsim: development of a Monte Carlo ray tracing software for the simulation of photoluminescent solar concentrators***

Miguel Valle del Olmo, **Characterization of external quantum yield and lateral energy losses in photoluminescent solar concentrators**

Remy Carera, Royal Institute of Technology, Stockholm, Sweden, **Towards corrosion-resistant low emittance coatings for unglazed facade collectors**

Martin Python, EPFL, **Fluorescence of quantum dots**

Visiting Students

Joel Chaney, University of Nottingham, UK, **Optical characterization of sol-gel deposited silicon and titanium dioxide films**

Deepanshu Dutta, Indian Institute of Technology IIT New Delhi, India, **Fabrication of multilayered thin film interference filters based on dielectric oxides prepared by the sol-gel method for a colored glazed thermal solar collector**

Hitesh Chelawat, Indian Institute of Technology IIT Bombay, India, **Sol-gel deposition of porous silicon dioxide films**

Olivia Bouvard, Université Montpellier II, Institut Universitaire Technologique de Nîmes, **Couches minces sélectives pour capteurs solaires thermiques**

Charudatta Galande, IIT Kanpur, India, **Synthesis of photoluminescent nanocomposite thin films for solar collectors**

Roopali Kukreja, IIT Mumbai, India, **Deposition and optical characterisation of thermochromic thin films based on vanadium oxide**

Technical support

Pierre Loesch, LESO

Dissemination

Documentary **NZZ Format: Sonne - Zukunftsenergie und Wirtschaftsmotor**,

- on Swiss German television channel **SF2**, 09/09/2007, 21.30h.
- on **VOX**, 08/12/2007, 9.10h

A considerable part of the movie concerning the topic of novel colored glazing for solar thermal facade collectors was shot in our laboratory. The movie is available on DVD from SF2.

J. Wellstein, **Viele bunte Kollektoren**, Erneuerbare Energien 11.12.2006, 7263 / 22, 1772

J. Wellstein, **Sonnenkollektoren mit farbigem Deckglas**, HL-Gebäudetechnik 2/2007

J. Wellstein, *Davantage d'énergie solaire grâce aux couleurs*, RTS Swiss Engineering, Dez. 2007, No. 12, page 18

J. Wellstein, *Mehr Farbe ist gefragt*, publications CH-Forschung 2006-2007 in the following newspapers: Altoggenburger, Anzeiger vom Rottal, Anzeige-Blatt Gais und Umgebung, Bulletin des SEV, Reussbote, Die Botschaft, Walliser Bote; (www.ch-forschung.ch)

J.-L. Vautravers, *Innovation mondiale à l'EPFL*, revue *Propriété*, octobre 2007 No. 10/2007

J.-L. Vautravers, *Innovation mondiale à l'EPFL*, Lausanne Cités, 31/10/2007

Awards

ABB Innovation Award 2007

Andre Kostro, *Photonsim: development of a Monte Carlo ray tracing software for the simulation of photoluminescent solar concentrators*

Solar Energy Journal Best Paper Award 2005 - 2007

ISES world congress 2007, Beijing, China

Best Full Length Paper in Energy Conversion:

Nanostructured materials for solar energy conversion

Peter Oelhafen and Andreas Schüler

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