Annual Report 2004, December 2004

Project
Colored Solar Collectors
Capteurs Solaires en Couleur

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SFOE Project-No.	43971
duration of project	Phase II: 01/02/2004 - 15/12/2006

SUMMARY

The architectural integration of thermal solar collectors into buildings is often limited by their black color, and the visibility of tubes and corrugations of the absorber sheets. A certain freedom in color choice would be desirable, but the colored appearance should not cause excessive performance degradation. Multilayered thin film interference filters on the collector glazing can produce a 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 shall be manufactured by the sol-gel dip-coating process. The proposed colored glazed solar collectors will be ideally suited for architectural integration into buildings, e.g. as solar active glass facades.

The sol-gel fabrication of interference stacks of up to five layers of silicon and titanium oxide films could be demonstrated in the laboratory, in the first step on microscope slides. Optical measurements are used to determine film thicknesses and optical constants of the individual layers, and to measure color coordinates and solar transmission for the multilayer stacks. The solar transmission of such samples can be improved by titanium silicon mixed oxides, which could have been synthesized by the sol-gel method. Hereby the compatibility problems of the originally used solution have been solved, and the refractive index of the resulting mixed oxide can be perfectly controlled by tuning the atomic concentration ratio of silicon and titanium.

One of the main technical risks is related to the fact that for a convincing demonstration of the idea high quality coatings are absolutely necessary. Therefore visible defects induced during the dip-coating process by dust particles in the atmosphere or in the used solutions must be imperatively avoided, as well as thickness variations due to vibrations.

After optimizing various aspects of sample preparation, processing and handling, high-quality multilayered coatings could finally be produced on an intermediate size scale (6 cm x 7 cm), opening up the way to samples with suitable quality and sizes large enough for a convincing demonstration of the idea.

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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, limits the architectural integration into buildings. A recent opinion poll [1] showed that 85% of architects would prefer different colors besides black, even if a lower efficiency was the price to pay.

In order to express the performance of a colored solar collector, a figure of merit M as the ratio of the relative luminosity R_{VIS} and the solar energy losses by reflection R_{sol} has been defined [2]. It can be shown that the principal upper limit for this figure M amounts approximately to the value six, which allows strikingly low energy costs per perceived brightness.

Several research groups 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. Interference colors of dielectric thin films are ideally suited for this purpose, as proposed in a recent feasibility study [2]. 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 shall be manufactured by the sol-gel dip-coating process. The latter will allow the production of samples large enough for demonstration (size A4) without the necessity of expensive large-scale vacuum equipment.

Goals for 2004:

- establishing the **infrastructure** for **sample fabrication** on intermediate size scale (6 cm x 7 cm)

- building **experimental setups** for **angle-dependent** spectral transmittance and reflectance measurements

- **validation** of the experimental methods

- development of strategies for **refractive index determination**

- sol-gel deposition of **SiO_2//TiO_2 multilayers** on small substrates (microscope slides)

- deposition of SiO_2//TiO_2 multilayers in **sufficient quality** on substrates of intermediate size

Activities and Results

1. Establishing the Experimental Infrastructure

1.1 Bakeout container for intermediate sample size (6 cm x 7 cm)

A dust-sensitive dip-coating process is used for the deposition of thin film coatings on solar collector glasses. Hereby a laminar flux-chapel provides a controlled, particle-free atmosphere. After dip-coating, the thin film samples are tempered in a laboratory oven. For the production of multilayered interference coatings, alternating dipping and tempering steps are repeated, implying the necessity for dust-protection of the samples during transfer and tempering.

For samples of the intermediate size (6 cm x 7 cm), a special sample container has been conceived and built (see fig.1). Coated samples are hold only by the edges, thus avoiding any degradation of the coating by mechanical contact. In order to also insure a good homogeneity also of the temperature distribution during the tempering process, samples are supported by thermally insulating glass rods at the bottom.

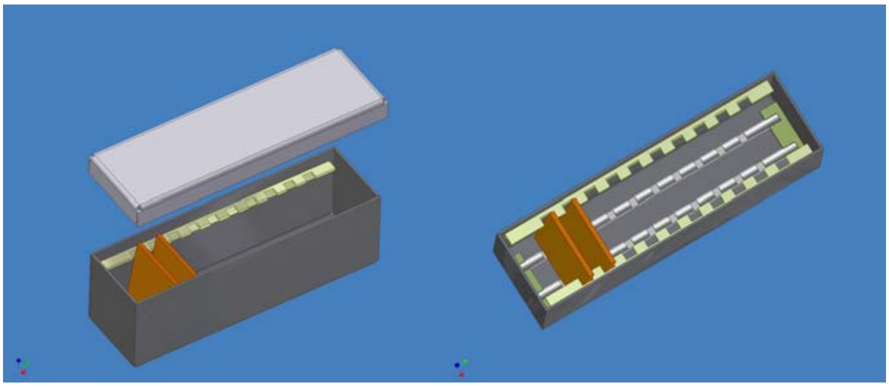


Fig.1: Bakeout container for tempering samples of intermediate size (6 cm x 7 cm). After dip-coating in the laminar flux chapel, samples are dust-protected during tempering in the oven. Samples are hold only by the edges, thus avoiding any degradation of the coating. In order to insure a good homogeneity also of the temperature distribution during the tempering process, samples are supported by thermally insulating glass rods at the bottom.

1.2 Set-ups for spectral measurements of angle-dependent transmittance and reflectance

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 [see fig.2a)]. 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 conceived and constructed [see fig.2b)]. 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.

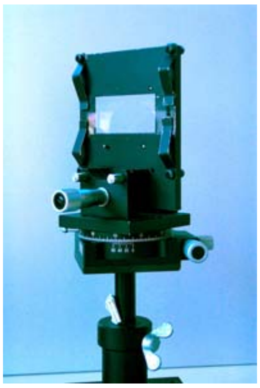
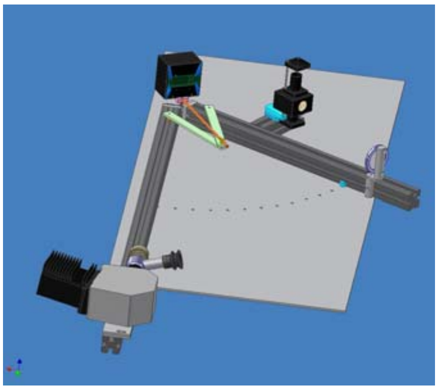
a)  b) 

Fig.2: a) Sample holder for transmittance versus angle measurements. The angle of incidence can be set very accurately. b) Apparatus for the variable angle reflectance measurements. A special mechanism guarantees the alignment of the sample.

2. Validation of Experimental Methods

2.1 Spectrophotometry

When a diffraction grating is used for spectrophotometry, it should be verified that the measured signal is not perturbed by higher order diffraction. Order-sorting filters allow the suppression of such errors.

An example for the technique is shown in fig.3. In order to measure in a wide range, two spectra are acquired from a thin film sample (titanium dioxide on glass), with and without a red filter (instrument: *ORIEL MS 125*^{TM} *1/8m Spectrograph, InstaspecTM II Photodiode Array Detector*). 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).

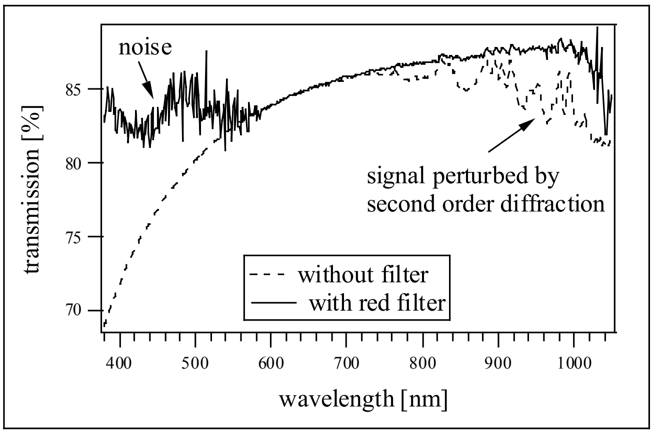
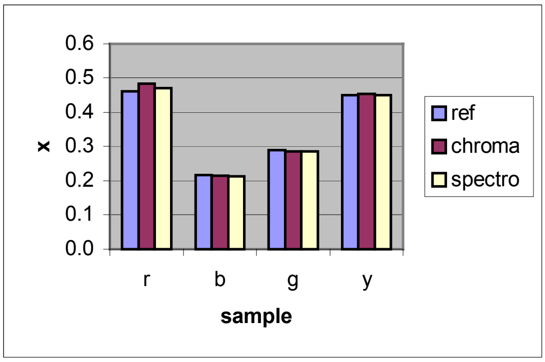


Fig.3: Transmission spectra of a TiO_2 film on glass measured with and without a red filter. The spectrum measured without filter shows a second order diffraction signal above 700 nm. The red filter cuts the radiation with wavelengths below 550 nm. Consequently, also the second order signals are suppressed up to a wavelength of 1100 nm.

2.2 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 125^{TM} 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.4 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.



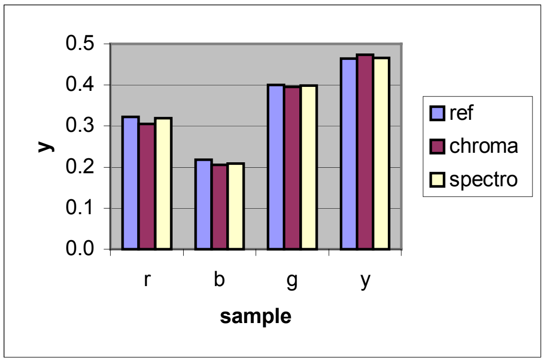


Figure 4: CIE color coordinates x and y, as determined for four reference samples (colors red, blue, green and yellow, denoted as r, b, g, y) by the Minolta instrument (chroma) and by the spectrophotometer with integrating sphere (spectro). The measured values are compared to the reference values provided 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.

2.2 Solar Simulator

A method of measuring directly the solar transmittance 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 *4495*0

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*). The results are displayed in table **I**.

Filter combination 2 seems to be most suitable for this measurement. The deviations from the spectrophotometrically determined values amount only to approx. 1 % .

Sample	**Spectrometer Basel Varian CARY 5 Transmission [%]**	**Solar simulator Filter combination 1 Transmission [%]**	**Solar Simulator Filter combination 2 Transmission [%]**
A	92	92	91
B	89	87	88
C	87	85	86
D	90	90	89
E	85	82	84
F	82	81	82

Table I : Solar transmission factors for multilayered sputtered thin films samples (A to F) obtained by different methods. Spectrophotometric measurements have been performed at the University of Basel using the instrument Varian CARY 5 . The adjacent columns show values obtained by the solar simulator in combination with the radiation power meter using different filter combinations.

3. Strategies for Refractive Index Determination

3.1 Method of extrema for relatively thick films

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 (delta R) to the difference in refractive index (delta n) between substrate and film is illustrated in fig.5a). 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.5b). 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.

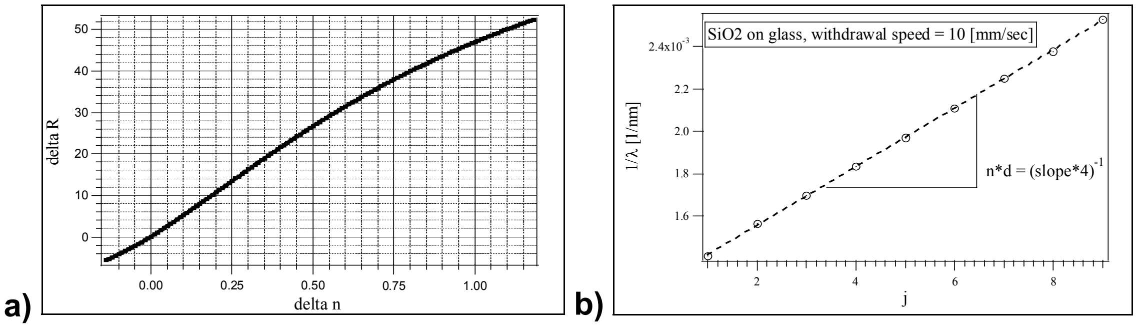


Fig.5: a) Relation of the intensity difference of the minima and maxima in the transmittance or reflectance spectra to the difference in refractive indices of film and substrate. b) Positions of maxima and minima in the transmission spectra of a SiO_2 film are plotted vs. the number of order j . The graph exhibits nearly perfect linear behavior. The slope of the plot yields a value for the optical path nd.

3.2 Method of angle-dependent measurements for relatively thin films

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. An example is shown in fig.6a) (thin titanium dioxide film on glass). The resulting curves can be used as target values for a numerical least square fit performed by a special software (TFcalc), yielding a value for the refractive index n at each considered wavelength [see fig.5b)]. 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.

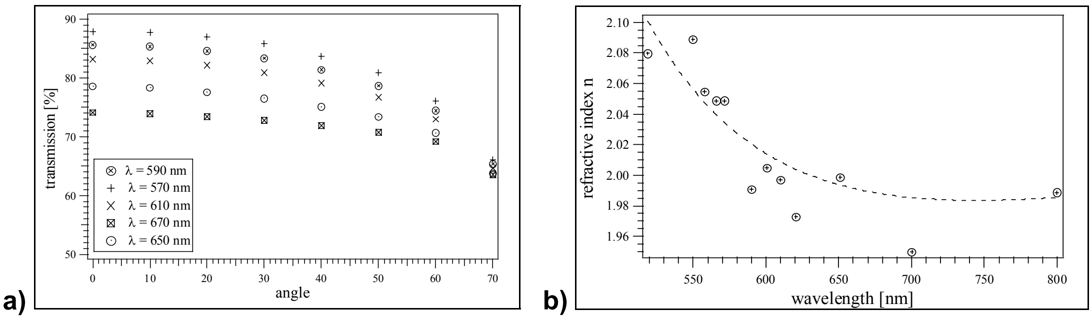


Fig. 6: a) Angle-dependent transmittance values for a selection of different wavelengths. Each data set is imported into the simulation software TFCalc as target values for the determination of the refractive index and the film thickness. b) Dispersion relation inferred from the measured values shown in a). A Cauchy dispersion relation has been fitted to the refractive index data.

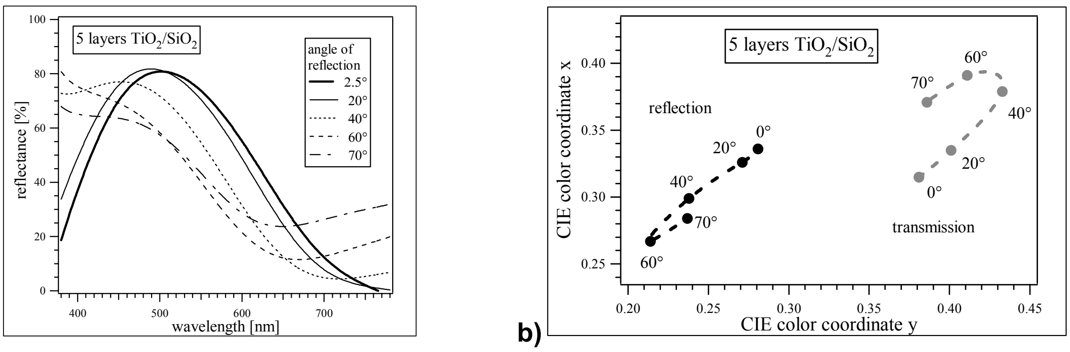
4. Sol-Gel Deposition of SiO_2//TiO_2 multilayers on small substrates (microscope slides)

Multilayered interference stacks of alternating titanium and silicon oxide thin films have been produced by successive dip-coating and tempering steps. As it happens naturally in the dip-coating process, the substrates have been coated on both sides. The thicknesses of the individual layers have been controlled by tuning the withdrawal speed and the solution concentration in the sol-gel dip-coating process. The thickness of the titanium dioxide layers amounts to 44 nm, the thickness of the silicon dioxide layers to 120 nm. Adding layers successively leads to an increase in visible reflectance R_{VIS}, and in the energy-effectiveness M of the colored reflection (see table II). Already for a three-layered coating, the colored reflection is stronger than needed, but the solar transmission drops down to 74%. Computer simulations showed that the solar transmission can be kept high if intermediate refractive index materials were available, motivating the experiments regarding the deposition mixed titanium silicon oxides (see description below).

The angular dependence of the colors has been characterized using the experimental set-ups described above. Fig.7a) shows the measured angle-dependent reflectance spectra for a five layered sample. The derived color coordinates x and y for reflectance and transmittance are illustrated in Fig.7b).

number of layers	0	2	3	5
R_{VIS}	8	20	56	70
T_{sol}	92	87	74	75
M	1	1.5	2.2	2.8

Table II : Values of visible reflectance R_{VIS} , solar transmittance T_{sol} , and energy-effectiveness of the colored reflection M = R_{VIS} / (100% - T_{sol}) , as determined for multilayer stacks of alternating titanium oxide and silicon oxide thin films, with 2,3 and 5 layers (0 layers: uncoated substrate).



a) b)

Figure 7: a) Angle-dependent transmission spectra for a 5 layered stack of alternating titanium and silicon dioxide thin films. b) Angle-dependent color coordinates of reflectance and transmittance, as determined for the same sample.

5. Sol-Gel Deposition of $Ti_{1-x}Si_xO_2$ mixed oxides on small substrates (microscope slides)

In order to attain a high solar transmittance in combination with a high energy-effectiveness of the colored reflectance, the use of intermediate refractive index materials, such as mixed titanium silicon oxides, is necessary. The compatibility problems of the originally used 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 be possible. Hereby the refractive index of the mixed oxides can effectively be controlled by the concentrations of the ingredients. Fig.8 illustrates the dispersion relations obtained from a series of samples with varying atomic concentration ratio of titanium and silicon. These results have to be considered as a major breakthrough opening up manifold possibilities and considerable freedom in coating design.

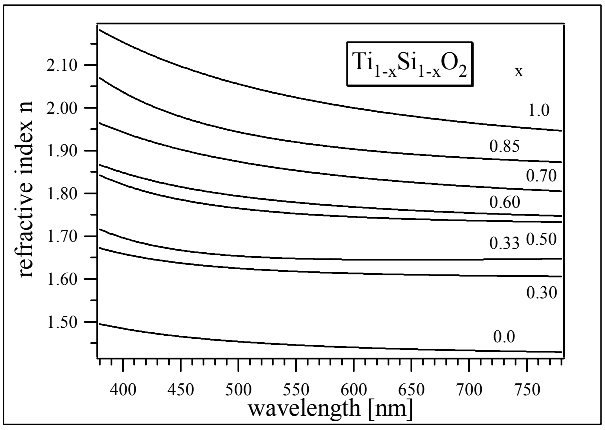


Fig. 8: Dispersion relations n(λ) for sol-gel deposited mixed titanium silicon oxide films, as determined by spectrophotometry.

6. Deposition of high quality SiO_2//TiO_2 multilayers on substrates of intermediate size (6 cm x 7 cm)

One of the main technical risks of the project is related to the fact that for a convincing demonstration high quality coatings are absolutely necessary. Therefore visible defects induced during the dip-coating process by dust particles in the atmosphere and in the used solutions must be imperatively avoided, as well as thickness variations due to vibrations.

After optimizing various aspects of sample preparation, processing and handling, high-quality multilayered coatings could finally be produced on an intermediate size scale. Conventional float glass of a thickness common for real-size application has been used as substrates, with dimensions of 4mm x 60 mm x 70 mm. The fabricated multilayer stacks consist of alternating titanium and silicon oxide thin films. After first attempts yielding a rather poor quality of the coatings, all steps involved in the process have been investigated thoroughly, and improved where necessary. Care has to be taken in substrate pre-treatment, preparation of clean and particle-fee solutions, and vibration-free withdrawal of the substrates after dipping. By adapting the concentration of the used solutions, withdrawal speeds can be kept above a threshold of 1 mm/sec, rendering the process less sensitive to vibrations. For multilayer fabrication, care has to be taken to immediately dissolve the last drop sticking to the bottom of the sample after withdrawal, otherwise the additional relatively thick xerogel residue will be transformed into dust during bakeout.

The quality of the finally deposited multilayered coatings of alternating titanium and silicon dioxide is illustrated by fig.9. Shown are coatings consisting of stacks of three, four and five individual layers. No defects due to dust particles are visible. Except for the common effect at the edges (the edges are usually cut off in an industrial process), the coatings are very homogenous.

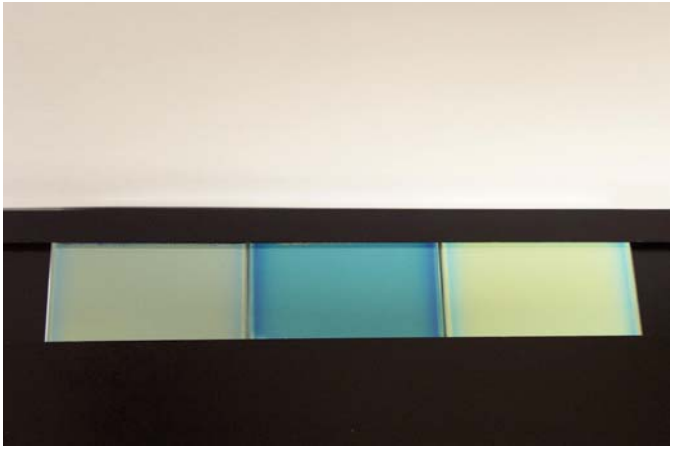


Fig.9: Multilayers of thin oxide films on glass substrates produced by the sol-gel dip-coating process in a laminar-flux chapel. Coating defects are avoided by a careful substrate pretreatment, clean solutions, and the particle free controlled atmosphere. From left to right: stacks of three, four and five layers.

National Collaboration

A close collaboration exists with the research group of Prof. Peter Oelhafen, Institute of Physics, University of Basel. Especially mentioned should be the contribution of Jamila Boudaden. The collaboration can be characterized as cooperative and productive.

International Collaboration

Our research group at LESO/EPFL is involved in the European Project *SOLABS*, with 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

Evaluation 2004 and Outlook 2005

The project has been extremely successful in 2004. Especially one of the main technical risks of the project, related to the quality of the coatings produced by sol-gel dip-coating, became under control. With the equipment conceived and constructed at LESO, multilayered interference coatings free of visible defects could be produced.

All project goals for 2004 have been accomplished:

Establishing the **infrastructure** for **sample fabrication** on intermediate size scale (6 cm x 7 cm):
- a special bakeout container has been conceived and built for dust-protection of the samples during transfer and tempering

Building **experimental setups** for **angle-dependent** spectral transmittance and reflectance measurements:
- a new sample holder permits angle-dependent spectral transmittance measurements
- a new experimental setup for angle-dependent spectral reflectance measurements has been built

Validation of the **experimental methods**:
- the method of suppressing signal contributions due to higher order diffraction has been validated for spectrophotometry
- the determination of color coordinates by spectrophotometry has been cross checked with other methods
- the direct determination of the solar transmittance by solar simulator and thermopile detector has been cross-checked with spectrophotometry in Basel

Development of **strategies** for **refractive index determination**:
- strategies for film thickness and refractive index determination have been elaborated for the two cases of relatively thick and relatively thin films

Sol-gel deposition of **SiO_2//TiO_2 multilayers** on **small substrates** (microscope slides):
- multilayered coatings of alternating titanium and silicon dioxide could be deposited with up to five individual layers
- coatings exhibit a good energy-effectiveness of the colored reflection
- visible reflectance stronger than necessary, solar transmission should be increased
- angle-dependent color coordinates determined

Deposition of **SiO_2//TiO_2 multilayers** in sufficient quality on substrates of **intermediate size**:
- new bakeout container permits sample production of high quality
- samples free of visible defects due to dust particles
- good film homogeneity achieved

In addition to the project goals planned for 2004, further progress has been made: **mixed titanium silicon oxide films** could already be deposited on microscope slides. A smooth variability of the refractive index in the range from approx. 1.5 to 2.1 (at 550 nm) opens up manifold possibilities and considerable freedom in coating design.

Topics for 2005:

- **multilayers** of **mixed** titanium silicon **oxides**
- feasibility study on sol-gel deposition of **fluorides**
- multilayers on large scale (**substrate size A4**)

Publications 2004

Schüler A., Roecker C., Scartezzini J.-L. (EPFL), Boudaden J., Videnovic I.R., Ho R.S.-C., Oelhafen P.,
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Dielectric interference layers for solar thermal collectors,
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Oral Presentations 2004

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

Dutta D., ***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

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

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

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

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

Poster Presentations 2004

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

Diploma Work in Progress (related topics)

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

Deepanshu Dutta, Indian Institute of Technology IIT New Delhi, India

Joel Chaney, University of Nottingham, UK

Technical support

Pierre Loesch, LESO

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