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Feasibility study on the sol-gel deposition of nanostructured materials based on oxides and fluorides for coatings on solar collector glazing

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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 the choice of color 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. The proposed colored glazed solar collectors will be ideally suited for architectural integration into buildings, e.g. as solar active glass facades.

Suitable interference filters have been designed and optimized by numerical simulation and shall be manufactured by the sol-gel dip-coating process. The refractive index of the thin film materials should ideally be **tunable** in a large range. Above all the availability of **low values of the refractive index** favors a high solar transmittance which is essential for the application in solar collector glazing. Thin film materials with lower refractive index than that of SiO_2 are also useful for the application as **anti-reflection coatings** on collector glazing. In order to achieve the continuous control of the refractive index, constituents of different refractive indices shall be mixed in varying concentrations. Hereby light scattering has to be avoided, which implies a need for particles sizes much smaller than the occurring wavelengths of light. The corresponding thin films should therefore consist of **nanostructured** materials. Aiming at a large range of refractive indices, mixtures of the low-index material SiO_2 and the high-index material TiO_2 shall be studied ($Ti_xSi_{1-x}O_2$ thin films). In order to achieve a lower refractive index than that of SiO_2 , the possibility of creating voids (porous SiO_2) shall be studied. MgF_2 is a compact but soft material with refractive index lower than that of SiO_2. A sol-gel method for MgF_2 synthesis shall be developed and the necessity of an inert gas atmosphere during the annealing process shall be investigated. Finally it shall be investigated, whether a tunable low-index system can be achieved by quaternary films based on Mg, F, Si and O.

The **sol-gel deposition** of all proposed materials **has been demonstrated successfully**. A **continuous control** of the refractive index and **values considerably lower than for SiO_2** have been achieved.

Introduction

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 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 [2,3]. 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 shall be manufactured by the sol-gel dip-coating process. Sol-gel dip coating does not require expensive vacuum equipment, and is already in use for the industrial production of anti-reflection coatings.

In order to fabricate the designed interference multilayer stacks, a large range of available refractive indices is desirable. Ideally, any desired refractive index within this range should be accessible. Preliminary simulations [4,5] 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. 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.

Aiming at a continuous control of the refractive index, constituents of different refractive indices shall be mixed in varying concentrations. Hereby light scattering has to be avoided, which implies a need for particle sizes much smaller than the occurring wavelengths of light. The corresponding thin films should therefore consist of **nanostructured** materials (for a recent review of the application of nanostructured materials in solar energy conversion see e.g. ref. [6]).
Targeting a large range of refractive indices, mixtures of the low-index material SiO_2 and the high-index material TiO_2 shall be studied (**$Ti_xSi_{1-x}O_2$** thin films). By producing gold nanocrystals in SiO_2, a model system for validating the envisaged analytical techniques (electron microscopy, electron diffraction and X-ray diffraction) shall be synthesized (**SiO_2:Au**). For example, from the high difference in atomic number between Au and Si or O, a high contrast for electron microscopy can be expected. In order to achieve a lower refractive index than that of SiO_2, the possibility of creating voids (**porous SiO_2**) shall be studied. **MgF_2** is a compact but soft material with a refractive index lower than that of SiO_2. A sol-gel method for MgF_2 synthesis shall be developed and the necessity of inert gas atmosphere during the annealing process shall be investigated. Finally it shall be investigated, whether MgF_2 and SiO_2 can be mixed to form a **nanocomposite** material Mg:F:Si:O which might represent a tunable low-index system.

Within this study the feasibility of the sol-gel deposition of the following materials shall be investigated:

- $Ti_xSi_{1-x}O_2$ (large range of refractive indices)
- SiO_2:Au (model system for validation of analytical techniques)
- porous SiO_2 (lower refractive index by introduction of voids)
- MgF_2 (compact but soft material with refractive index lower than that of SiO_2)
- Mg:F:Si:O (tunable low-index system)

Goals:

- refractive index **n continuously tunable** in a wide range
- achieving **n values lower than for SiO_2**

Technical challenges:

- solving compatibility problems occurring during mixing of precursor solutions
- development of new precursor solutions for fluorine based materials
- avoiding hydrofluoric acid HF
- achieving good wettability of the substrate by the solutions
- formation of non oxidized inorganic compounds during annealing step in inert gas or air

Results

1. Titanium silicon mixed oxide ($Ti_{1-x}Si_xO_2$)

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 [4]). Mixtures of those 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. Hereby the refractive index of the mixed oxides can effectively and continuously be controlled by the concentrations of the ingredients. Fig.1 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.

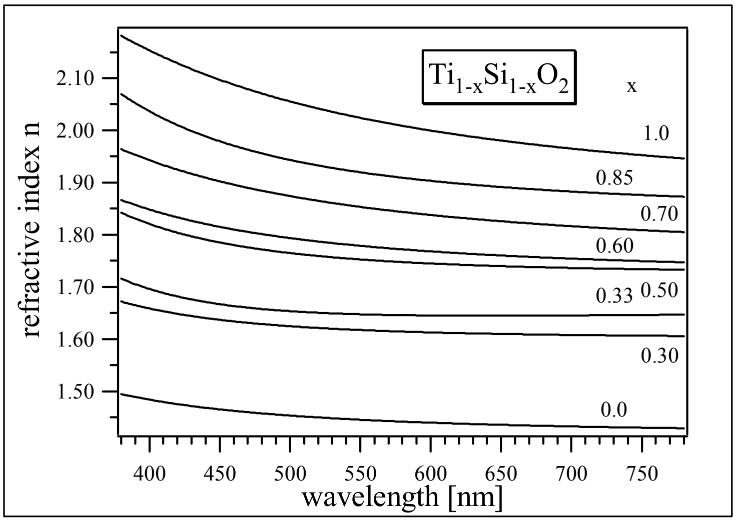

Fig. 1: Dispersion relations n(λ) for sol-gel deposited titanium silicon oxide films, as determined by spectrophotometry. Most presumably these films consist of TiO_2 nanocrystals being imbedded in an amorphous SiO_2 matrix.

2. Gold containing silicon dioxide (SiO2:Au)

SiO_2:Au films are perfectly suited for testing the envisaged analytical techniques such as electron microscopy, electron diffraction and X-ray diffraction. The precipitation of nanometer-sized gold aggregates has been achieved by adding $AuCl_4$ to the precursor solution. The gold nanocrystals have been resolved by transmission electron microscopy TEM, confirming that nanostructures can be produced on large areas by simple sol-gel dip coating. Fig. 2a) shows a view of a thin film deposited on a coated copper TEM grid (viewing axis perpendicular to thin film plane). Fig. 2b) shows a side-view of a cleaved sample (thin film on silicon 100 substrate, viewing axis in film plane). The fringes observed in the region of the Si substrate are due to electron interference.

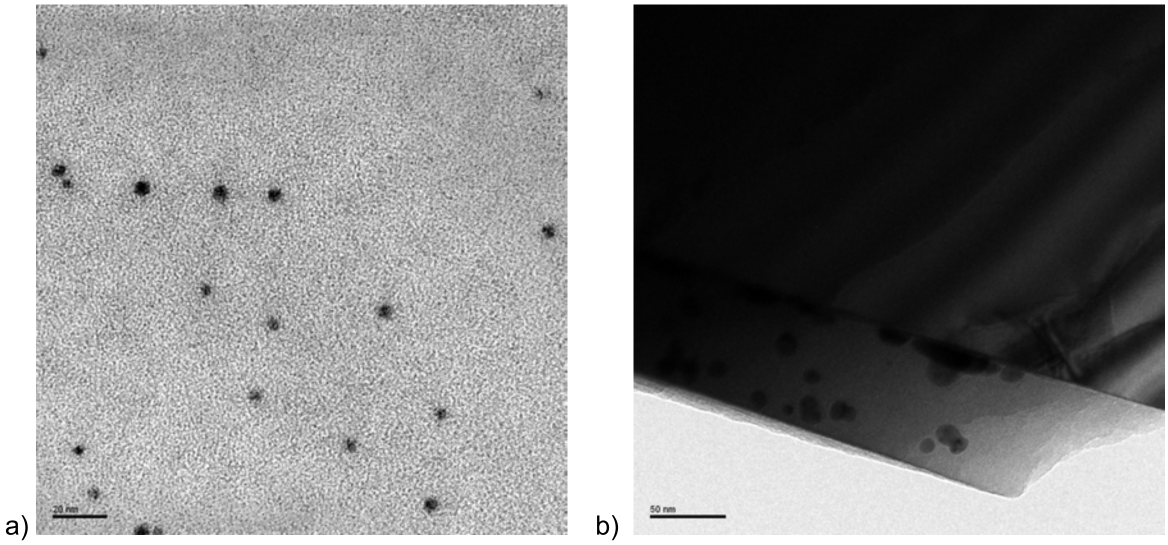

Fig.2: a) Transmission electron microscopy of a thin SiO_2:Au film deposited on a coated copper TEM grid. The viewing axis is perpendicular to thin film plane. Gold nanoparticles can clearly be resolved. b) TEM side-view of a cleaved sample. The 75 nm thin SiO_2:Au film was deposited on a silicon 100 substrate. The viewing axis is in the film plane. The gold aggregates close to the interface seem to be larger than those in the volume of the thin film.

3. Porous silicon dioxide

Most dielectric thin film materials exhibit a higher refractive index than that of SiO_2. One way to achieve a lower refractive index 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 shall be created which contain nanometric organic regions. In the subsequent annealing step, the organic macromolecules shall be oxidized, leaving behind nanopores.

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. 3 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 550nm surpasses 98.5%.

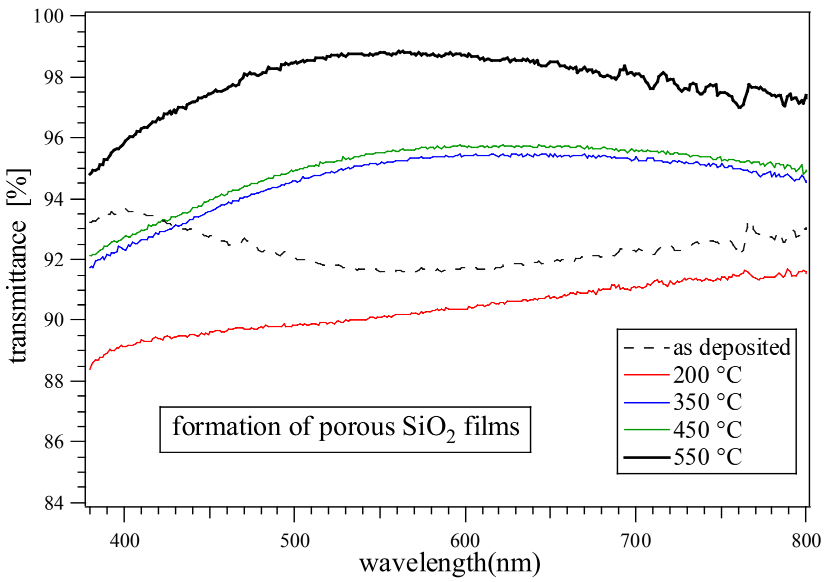

Fig.3: Evolution of normal transmittance spectra during pore formation (spectra as deposited and after one annealing step at 200°C, 350°C, 450°C and 550°C, respectively). After tempering at 550°C the spectral transmittance at wavelengths around 550nm surpasses 98.5%.

4. 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 be 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. 4 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.

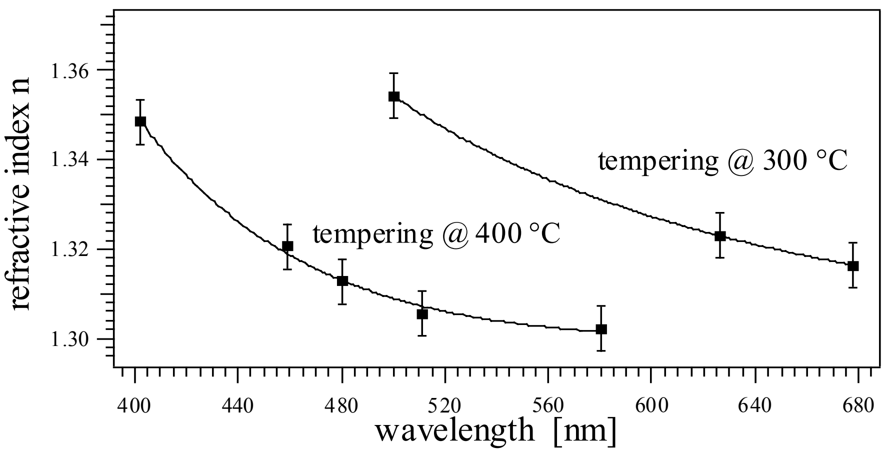

Fig.4: Dispersion relation $n(\lambda)$ of sol-gel deposited MgF_2 films. A dependence of the refractive index on the annealing temperature is observed, rising the question whether at 400°C a small volume fraction of pores is formed.

5. Quaternary films based on Mg, F, Si and O (Mg:F:Si:O)

Magnesium fluoride MgF_2 is one of the rare thin film materials in use exhibiting a refractive index lower than that of SiO_2. Its application though is restricted 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. 5 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).

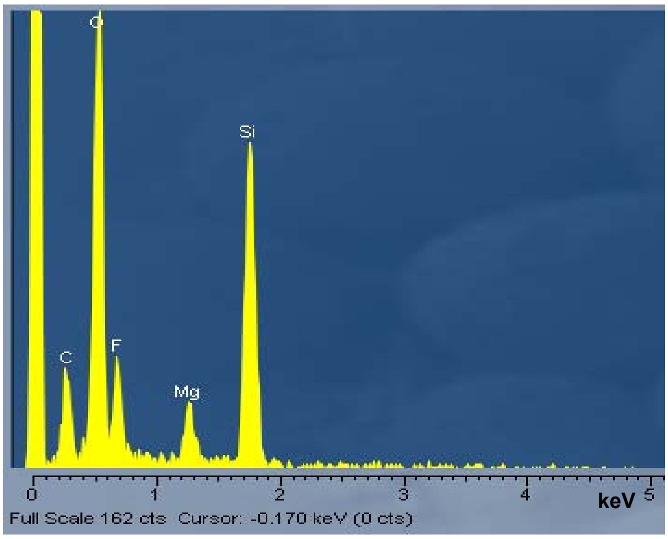

Fig. 5: Energy-dispersive X-ray microanalysis of a quaternary thin film. The characteristic emission lines for the elements confirm the presence of Si, O, Mg, and F. The line attributed to carbon is most presumably due to surface contamination by hydrocarbons.

The refractive index of the thin films has been determined and plotted for a wavelength of 685 nm as a function of the chemical composition (see Fig. 6). Values considerably lower than that of pure SiO_2 have been achieved, the lowest for equal molar concentrations of Si and Mg (corresponding to 50% molar fraction SiO_2). In order to explain this minimum of the refractive index at equal molar concentrations of Si and Mg, further investigations of the morphology and nanostructure of such films are necessary. Possible explanations might be the occurrence of nanometric pores or the formation of ternary or quaternary phases.

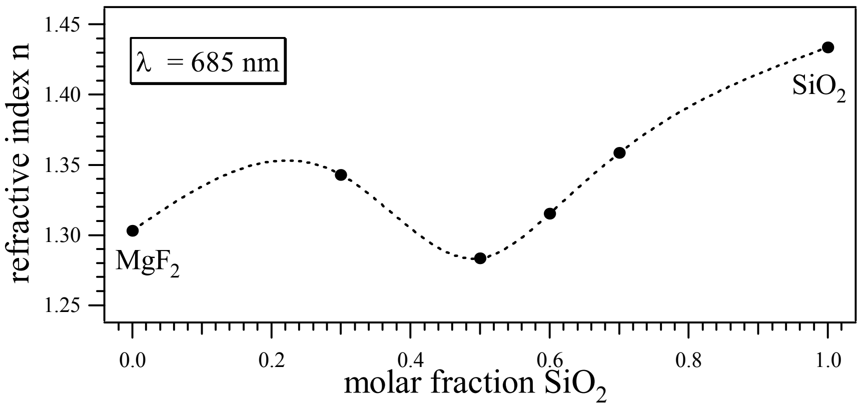

Fig. 6: Refractive index at 685 nm as a function of the chemical composition of quaternary thin films based on the elements Mg, F, Si, and O. Values considerably lower than that of pure SiO_2 have been achieved, the lowest for equal molar concentrations of Si and Mg (corresponding to 50% molar fraction SiO_2). In order to explain this minimum of the refractive index at equal molar concentrations of Si and Mg, further investigations of the morphology and nanostructure of such films are necessary.

Conclusions

All envisaged materials ($Ti_xSi_{1-x}O_2$, SiO2:Au, porous SiO_2, MgF_2 and Mg:F:Si:O) could be prepared as thin films by sol-gel dip-coating and subsequent annealing.
Hereby all compatibility problems of the precursor solutions have been solved. Even for fluoride based films, the annealing step can be simply performed in ambient air and does not require complex installations for providing any inert gas atmosphere. The use of hydrofluoric acid HF can be avoided for the production of fluorine based coatings. $Ti_xSi_{1-x}O_2$ thin films offer a large range for continuous tuning of the refractive index. Gold containing silicon dioxide represents a model system perfectly suited for the validation of the envisaged analytical techniques. The structure formation on the nanometric scale has been imaged directly by electron microscopy. The refractive index of SiO_2 can be lowered considerably by the introduction of voids, resulting in highly transparent thin films. The durability of such films remains an issue (hardness, danger of pores filling up with hydrocarbons), as well as their applicability in multilayer stacks. Pure MgF_2 coatings represent a rather compact but soft material with a refractive index lower than that of SiO_2. The wettability of the used solutions appears somewhat critical and not always satisfying. In contrast to that, the wettability of the precursor solutions for quaternary Mg:F:Si:O films is much less critical, as well as haze formation during annealing. Such films represent a tunable low-index system, with a refractive index even considerably lower than expected. The coating hardness is most presumably clearly higher than that of pure MgF_2 and porous SiO_2 films. In addition, the risk of degradation by pore-filling is much lower than for porous SiO_2. However, the optical results imply that further studies of the nanostructure of this promising novel material will be necessary.

Exciting new possibilities for the development of single- and multilayered coatings on solar collector glazing have thus been opened.

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