Optical Properties of Thermochromic Granular Films

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Abstract

Abstract.. abstract.

1 INTRODUCTION

In the light of global warming, techlonogies that lower the overall energy consumptions, and thereby decrease energy-related carbon dioxide emmision, are more important today than in the past. Today the energy consumption of buildings in the developed contries constitute about 30-40% of their total energy usage and in humid regions, this increases to roughly 30% to 50% [3][4][5]. In 2010, 41% of the primary energy of the U.S. (being the second largest energy consumer globally), accounting for 7% of the global energy use, were consumed by the building sector. This resulted in approximately 40% of the total energy-related carbon dioxide emmision in the US. For comparison, the building sector in China accounted for 18% of the CO2 emmision of the country, whereas worldwide the building energy consumption is behind 8% of the total emmision. [2][6]. This motivates measures to be taken to reduce the building energy consumption, in order to reduce the related CO_2 emmisions.

Heating, ventilation and airconditioning (HVAC) help to maintain a comfortable indoor climate in buildings by compensating for heat loss through their envelope (walls, roof, windows or any element separating the indoor from the outdoor) or heating due to the thermal radiation from the sun. Together with lighting, they were responsible for about 60% of the total building energy consumption in 2010 (**???in the U.S. or in general???**). [2]. Considering thermal loss through the building envelope, the window elements are in fact the most energy inefficient components [7] and improving their thermal properties will be crucial in order to reduce the electricity costs. The thermal properties of the window depend mainly on the outdoor contidtions, shading, building orientation and type, in addition to the area of the window, its glass properties and glazing characteristics (13). In window standards, the latter is the most important, because the glazing characteristics includes thermal transmittance and ?solar parameters? *Not sure if I understand the meaning of solar parameters here*(14). **omformulere dette? sjekke hva det egentlig betyr? [1], s.354 avsnitt 2**
One way of improving the thermal effiency of the window is to add some additional mechanism, allowing the window to change its properties to the environment. An example of such improved windows are called "smart-" or "intelligent windows" and will be discussed in the next section.

EXTRA: Due to lighting, a window should be able to let through visible light (12).

- Two approaches to increase energy efficieny (7-10)
  - Active stratergies: improving HVAC systems and building lighting.
  - Passive stratergies: improving the thermal properties of the building envelope (elementss separating the indoor from outdoor), i.e. thermal insulation to wall, cool coatings on roofs and coated window glazings.

Smart Windows

Smart windows (or intelligent windows) are defined as a type of window that partially blocks the solar radiation in hot wather and transmitts the solar radiation in cold weather by changing its thermal and radiative properties dynamically(?trenger jeg "dynamically"? er ikke dette bare smør på flesk: changing+dynamically?) (25). The change in its optical properties can be obtained by adding a controllable absorbing layer on the surface of the glass (26). (The switchable reflective device (or dynamic tintable window)) The windows with the switchable layer can be categorized into active and passive systems. The active switchable glazing systems require an external triggering mechanism and offers supplementary options compared to passive systems. However, due to their dependency on a power supply and additional electronical curcuits makes them not as attractive as their passive counterparts. The passive devices do not require an external energy source, but switches automatically subject to environmental change. Examples of such devices are: photochomic windows reacting to light and thermochromic windows, which change in accordance to the temperature (11).

yyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyy
Maybe give example of active system, talk about lighting and then introduce Figure 1 and conclude that the TCW is the best low-priced alternative.(p.356).
yyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyy
(The information for this section was gathered by [1]) **FJERN DETTE eller INKLUDER DETTE PÅ EN BEDRE MÅTE (om det er verdt å nevne)**

[2]

REFERENCES

[1] Kamalisarvestani M, Saidur R, Mekhilef S, Javadi FS. *Performance, materials and coathing technologies of thermochromic thin films on smart windows*, PressOrSomething?, Renewable and Sustainable Energy Reviews ?? 2013; 26:353-364 ?? **ER DETTE RIGKTIG?**

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[4] Wilde PD, Voorden MVD.C. *Providing computational support for the selection of energy saving building components.* Energy and Buildings 2004;36(8):749-58

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2 SMART/INTELLIGENT WINDOWS

Requirements
Tell how

3   THERMOCHROMIC MATERIALS

Materials that change their optical nature when subject to irradiation by light(photons), temperature change or an applied electric field are called photochromic, thermochromic and electrochromic, respectively, and go under the gathered term chromic materials. ([2],1)

The word thermochromic originates from Greek, meaning warm or hot ("Thermos") and color ("Chroma"). As mentioned earlier, thermochromic materials their optical properties in response to changes in temperature and results in the material changing color ([**?**],74,75).

Typically, this change in color happens gradually over a range of temperatures. In this case it is called continuous thermochromism. Discontinuous thermochromism also occurs and involves a structural phase change at a certain characteristic "transition temperature" T_t ([2], 1).

What happens is that the thermochromic material is initially in its monoclinic state (cold state), where it behaves as a semiconductor being less reflective especially in the near-infrared(IR) region. Heating (**?This is a legit word right?**) the material, it will at a certain temperature, known as the transition temperature, change from the monoclinic state to a rutile state. In its rutile state (hot state) the material acts like a semi-metal, reflecting a wide range of solar radiation. This change of state is called metal-to-semiconductor transition (MST) ([**?**],76) and is fully reversible, **???** co-occured with large variations in both electrical and optical properties in the near-IR range (83). **??? -> check if understood and correctly written. E.g. what is co-occured?**

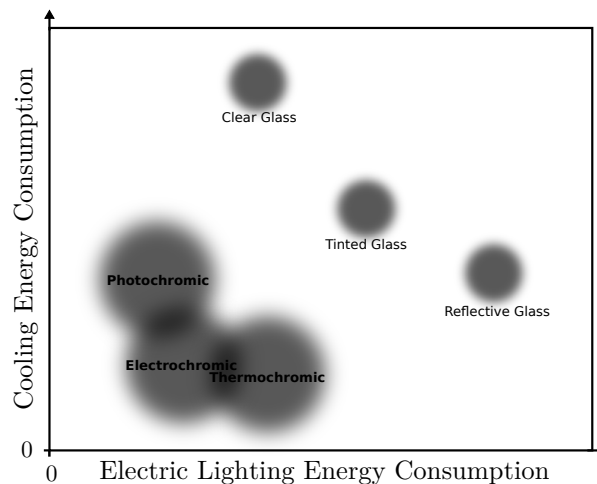(Main articles from section was based on [1] and [2])

4   THERMOCHROMIC WINDOWS

Figure 4.1: Comparison of the electric lighting energy and cooling energy consumption between different glazing types. Adapted from ([1],24). CHECK THIS!!: I understand that this graph shows the energy consumption of buildings using using different glazing for their windows, i.e. the window glazing impact of the building energy consumption; CHECK END. Also, I just drew the graph as good as I could from Kamalisarvestani2013. Is it still okay to use it? Should I comment on it not being exact (in case someone try to use data or something, I don't know)?

Disposition:
Requirements
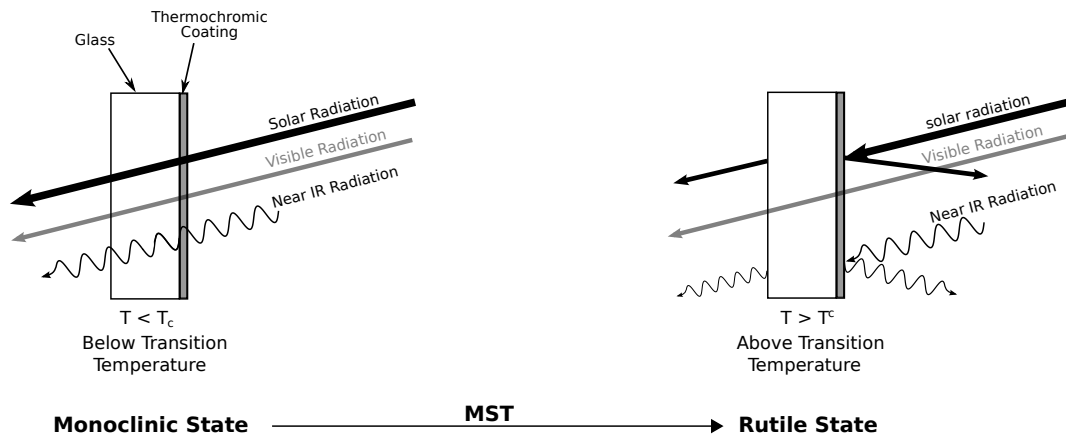- Ideal behavior- RADIATION FIGURE and PICTOGRAM

Figure 4.2: Schematic representation of thermochromic materials applied as an intelligent window coating [?].
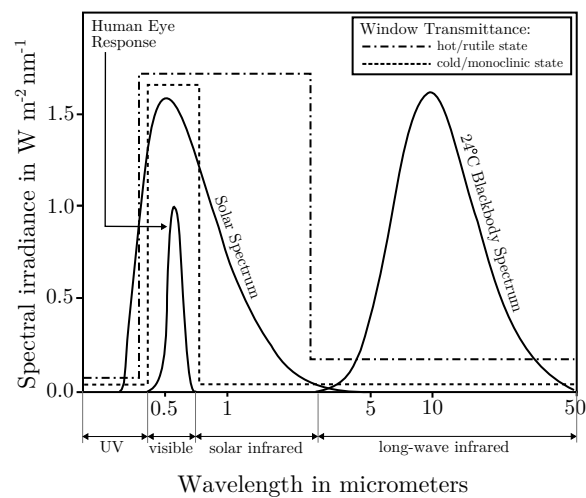

Figure 4.3: The spectral transmittance of a perfect thermochromic window, shown for both cold and hot environments (the monoclinic and rutile state, repsectively). Adopted from [1] [1]

- ambient transition temperature
- 60% transmittance in visible range, for lighting
- *Doping
- *Stress/strain
- *thickness

- price and mass producable: materials used and current technology

Best Candidates:
(strengths and weaknesses)
-VO2
-etc...

4

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[1] McCluney R, Center FSE. Fenestration solar gain analysis. Citeseer 1996.

[2] Kiri P, Hyett G, Binions R. Solid state thermochromic materials. Advances Material Letters 2010;1(2):20.

5   THEORY

To understand the theoretical background behind GranFilm and scattering on diffuse surfaces, it is convenient to start with the simple case of scattering on a flat interface of two different half-infinite media, see Figure !!FIGUREREF HERE!!.

The electric permittivity ε and magnetic permeability μ of the media are given with subscript 1 for the above media, and 2 for the media below. Using Maxwell's equations

$$\nabla \cdot \boldsymbol{D} = \rho_f \qquad\qquad \nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t} \tag{5.1a}$$

$$\nabla \cdot \boldsymbol{B} = 0 \qquad\qquad \nabla \times \boldsymbol{H} = \boldsymbol{J}_f + \frac{\partial \boldsymbol{D}}{\partial t}, \tag{5.1b}$$

where the electric fields, $\boldsymbol{E}$ and $\boldsymbol{D}$, and magnetic fields $\boldsymbol{B}$ and $\boldsymbol{H}$ are related through

$$\boldsymbol{D} = \varepsilon \boldsymbol{E}, \qquad\qquad \boldsymbol{H} = \frac{1}{\mu}\boldsymbol{B} \tag{5.2}$$

(assuming linear media), the fields above $\boldsymbol{E}^+(\boldsymbol{r})$ and below $\boldsymbol{E}^-(\boldsymbol{r})$ the interface can be calculated for a incident place wave (same goes for $\boldsymbol{B}$, $\boldsymbol{D}$ and $\boldsymbol{H}$). So far, the boundary between the two half-infinite media has been considered to be a sharp, flat discontinuity in $\varepsilon(z)$ and $\mu(z)$. As soon as the surface roughness, thickness and/or impurities are taken into acount, the complexity of the problem increases.

From "GranFilm-Software-Article":
Information on the dieletric behavior of surfaes can often be obtained by measuring the Fresnel coefficients, such as reflection, transmission and absorption.
?p.2?: for a layer with thickness negligible compared to wavelength, we introduce surface susceptibilities which interconnect the fresnel coeff. and characterise the optical response of the surface. ?? DID I UNDERSTAND THIS CORRECTLY? ??
Since all the Fresnel coeff. can be expressed in terms of these surface susceptibilities, the main task consist of calculating these coefficients for the appropriate geometry.
Goal of GranFilm: to calculate ?surface-susceptibility-/fresnel-coefficients? and the associated measurableFresnel quantities for various surface layer geometries.

- GranFilm is free open-source software

5.1   MIE RESONANCES/ PLASMON ABSORPTION MODES

From "GranFilm-Software-Article":
when small metallic particles, the resonances can be absorbed by visible light and strongly affect the fresnel coefficients depending on the particle morphology.

5.2   QUASISTATIC APPROXIMATION

5.3   ELECTROMAGNETIC EXCESS FIELDS

From "GranFilm-Software-Article":
(Bedeaux and Vlieger)
Difference between the bulk extrapolated fields and the real fields. The BC at the dividing surface (which drive all fresnel coeff.) are given in terms of the integrated excess fields perpendicular to the surface.

Bedeaux and Vlieger → formalism of excess quantities (does not require exact knowledge of the near suface EM-field behaviour).

Excess fields are defined as the differene between the real fields and the bulk fields extrapolated to the surface. E.g. for the electric field $E(r)$ the excess quantity is defined as

$$E_{ex}(r) = E(r) - E^-(r)\theta(-z) - E^+(r)\theta(z), \tag{5.3}$$

where $\theta(z)$ is the Heaviside function and the superscript $\pm$ are used to indicate the region above (+) and below (-) the dividing interface at $z = 0$. The excess field is only significant close to the surface, since $E(r,\omega) \rightarrow \rightarrow E^\pm(r,\omega)$ for $z \rightarrow \pm\infty$.

QUESTION: Is the $E^\pm$ field solved for a infinite homogeneous medium of type (+) and (-) respectively OR the field in simple two media interface scattering?

From Leif Amund Lies Msc Thesis:

Since the excess fields will only be significant close to the surface, they may be thought of as perturbations to the simple case of flat interface. *OWN INTERPRETATION: This meas that the bulk fields are the fields created from scattering in the interface between two half-infinite media.*

Instead of tediously using the quasi-static-"no source"-BC, the excess fields defined as for the electric field above are inserted into the full Maxwell equations to derive new non-sharp boundary conditions. The result reads **From Leif Amund Lies Msc Thesis AND GranFilm-Article**:

$$\left[\boldsymbol{E}_\parallel^+(\boldsymbol{r}) - \boldsymbol{E}_\parallel^-(\boldsymbol{r}) \right]\Big|_{z=0} = i\omega\hat{z} \times \boldsymbol{M}_\parallel^s(\boldsymbol{r}_\parallel) - \nabla_\parallel P_z^s(\boldsymbol{r}_\parallel) \tag{5.4a}$$

$$\left[D_z^+(\boldsymbol{r}) - D_z^-(\boldsymbol{r}) \right]\Big|_{z=0} = -\nabla_\parallel \boldsymbol{P}_\parallel^s(\boldsymbol{r}_\parallel) \tag{5.4b}$$

$$\left[\boldsymbol{H}_\parallel^+(\boldsymbol{r}) - \boldsymbol{H}_\parallel^-(\boldsymbol{r}) \right]\Big|_{z=0} = i\omega\hat{z} \times \boldsymbol{P}_\parallel^s(\boldsymbol{r}_\parallel) - \nabla_\parallel M_z^s(\boldsymbol{r}_\parallel) \tag{5.4c}$$

$$\left[B_z^+(\boldsymbol{r}) - B_z^-(\boldsymbol{r}) \right]\Big|_{z=0} = -\nabla_\parallel \boldsymbol{M}_\parallel^s(\boldsymbol{r}_\parallel), \tag{5.4d}$$

which is derived in Vlieger and Bedaux's *Optical Properties of Surfaces* (p.21). Here the quantities with superscript s are the so-called excess polarization and magnetization densities

$$\boldsymbol{P}^s(\boldsymbol{r}_\parallel) = \left(\boldsymbol{D}_\parallel^s(\boldsymbol{r}_\parallel), \ -\varepsilon_0 E_z^s(\boldsymbol{r}_\parallel) \right) \tag{5.5a}$$

$$\boldsymbol{M}^s(\boldsymbol{r}_\parallel) = \left(\boldsymbol{B}_\parallel^s(\boldsymbol{r}_\parallel), \ -\mu_0 H_z^s(\boldsymbol{r}_\parallel) \right), \tag{5.5b}$$

and the quantities on the right hand side are the excess fields integrated along the z-axis,

$$\boldsymbol{D}_\parallel^s(\boldsymbol{r}) = \int_{-\infty}^{+\infty} dz \, \boldsymbol{D}_{ex,\parallel}(\boldsymbol{r}), \qquad\qquad E_z^s(\boldsymbol{r}) = \int_{-\infty}^{+\infty} dz \, E_{ex,z}(\boldsymbol{r}) \tag{5.6a}$$

$$\boldsymbol{B}_\parallel^s(\boldsymbol{r}) = \int_{-\infty}^{+\infty} dz \, \boldsymbol{B}_{ex,\parallel}(\boldsymbol{r}), \qquad\qquad H_z^s(\boldsymbol{r}) = \int_{-\infty}^{+\infty} dz \, H_{ex,z}(\boldsymbol{r}). \tag{5.6b}$$

OWN INTERPRETATION: These integrated excess quantities are equivalent of representing the the excess fields in a single Dirac term $\delta(z)$ located at the surface ($z = 0$), e.g. such that the electric field can be written as

$$E(r) = E^-(r)\theta(-z) + E^s(r)\delta(z) + E^+(r)\theta(z). \tag{5.7}$$

OWN INTERPRETATION: Demanding that this fullfuls Maxwell's Equations, one obtains the Equations in (5.4) *. OWN INTERPRETATION: The simplest way to link the Surface polarization and magnetization density to the extrapolated bulk fields(?Sigma indexed fields?)involves a symmetric constitutive tensor $\xi_e^s(\omega)$ (ref B,V-OPoS).*

$$\boldsymbol{P}^s(\boldsymbol{r}_\parallel) = \xi_e^s \left[\boldsymbol{E}_{\parallel,\Sigma}(\boldsymbol{r}_\parallel), \ -D_{z,\Sigma}(\boldsymbol{r}_\parallel) \right] \tag{5.8}$$

OWN INTERPRETATION: The above relation is restricted to non-magnetic materials, i.e. that $\boldsymbol{M}^s(\boldsymbol{r}_\parallel) = 0$. The Σ index denotes the arithmetic mean of the upper and lower bulk fields, e.g. $\boldsymbol{E}_{\parallel,\Sigma} = \left\{ \boldsymbol{E}_\parallel^+(\boldsymbol{r}_\parallel) + \boldsymbol{E}_\parallel^-(\boldsymbol{r}_\parallel) \right\}/2$. If the interface are z = 0 is isotropic and symmetric, the interfacial tensor ξ_e^s is diagonal:

$$\xi_e^s = \begin{bmatrix} \gamma & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \beta \end{bmatrix}. \tag{5.9}$$

Here the coefficients γ and β are called the (first-order) surface susceptibilities (or here, constitutive coefficients). The constitutive coefficients of second order, δ and τ describe a non-local dependence (??SPATIAL VARIATIONS IN THE EXCESS QUANTITIES??)

Fresnel Coefficients

...need to write some more here...

$$r_s(\omega) = \frac{n_- \cos\theta_i - n_+ \cos\theta_t + i(\omega/c)\gamma}{n_- \cos\theta_i + n_+ \cos\theta_t - i(\omega/c)\gamma} \tag{5.10a}$$

$$t_s(\omega) = \frac{2n_- \cos\theta_i}{n_- \cos\theta_i + n_+ \cos\theta_t - i(\omega/c)\gamma} \tag{5.10b}$$

$$r_p(\omega) = \frac{\kappa_-(\omega) - i(\omega/c)\gamma\cos\theta_i\cos\theta_t + i(\omega/c)n_- n_+ \varepsilon_- \beta\sin^2\theta_i}{\kappa_+(\omega) - i(\omega/c)\gamma\cos\theta_i\cos\theta_t - i(\omega/c)n_- n_+ \varepsilon_- \beta\sin^2\theta_i}, \tag{5.11a}$$

$$t_p(\omega) = \frac{2n_- \cos\theta_i\left[1 + (\omega/2c)^2\varepsilon_-\gamma\beta\sin^2\theta_i\right]}{\kappa_+(\omega) - i(\omega/c)\gamma\cos\theta_i\cos\theta_t - i(\omega/c)n_- n_+ \varepsilon_- \beta\sin^2\theta_i}, \tag{5.11b}$$

$$\kappa_\pm = \left[n_+ \cos\theta_i \pm n_- \cos\theta_t\right]\left[1 - \frac{\omega^2}{4c^2}\varepsilon_-\gamma\beta\sin^2\theta_i\right]. \tag{5.11c}$$

From Eq. (**??**)-Eq.(**??**) we can observe that p-polarized excite the surface in both parallel and perpendicular direction, relative to the surface.

$$5.4 \quad .$$

D'Alembert Operator $\square$

$$\square = \partial^\mu \partial_\mu$$

$$= \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} - \frac{\partial^2}{\partial z^2}$$

$$= \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2$$

Lorentz Gauge:

For Lorentz invariance, convenient to choose the Lorenz gauge:

$$\square \vec{A} = \left[\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right]\vec{A} = \mu_0 \vec{J}$$

$$\square \phi = \left[\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right]\phi = \frac{\rho}{\epsilon_0}$$

6 ARTICLE NOTES

6.1 THERMOCHROMISM

[2] **Intelligent Themochromic Windows**
The use of air-conditioning systems to maintain comfortable working and living environments has become more common [1]. This leads to an increase in hte use of electricity and a concurrent increase in carbon dioxide emissions and other atmospheric pollutants formed in the electricity generation process. A self-propagating cucle results, in which blobal warming due to increases in these greenhouse gases necessitates the increased use of air conditioning systems. Technology is thus required that can reduce the use of air conditioning commercial and residential buildings to help break this cycle.

(...) window coatings can reduce cooling costs or heating requirements [2]. Using thermochromic coatings as intelligent window coatings[1-7], which change their optical properties with temperature; usually related to a structural pase change on passing through a critical temperature T_c. Thermochromic coatings would be applicable to climates where there are extreme changes in temperature over the year, for example, central and northern Europe, Japan, the United States, and Canada, which have hot summers and cold winters.

Vanadium(IV) oxide; transition temperature $Tc = 68°C$; visually and infrared trasnparent belov $T_c \rightarrow$ solar radiation passes through, keeping the interior warm. Below T_c it becomes infrared reflective and preventing excessive heating, while remaining visually transparent.

Critical temperature for vanadium is too high, but this can be lowered to 25°C uing dopants ([9]), most efficiently with tungsten(loading of only 2 atom percent required), in thin films prepared by physical vapor deposition methods [10] and sol-gel spin or dip coating [11].

problem: low luminous transmittance of the glazing VO_2 film [10-13]. (could be solved with doping[4] or anti-reflective coating ([12])). Also one needs a method where the thin films of the material can be applied cheaply and efficiently to the glass ([17]).

(p.394) Discussion of MST(metal-to-semiconductor transition) of VO_2 and structure changes through the MST. Discussion involves structure figures.

Goodenough proposes antiferroelectric transition being the drivings force for the MST in VO_2. $\rightarrow$ two transition temperatures: one due to antiferroelectric distortion and one due to the crystallographic distortion.

The next paragraph explains how doping of various elements varies the MST temperature. The most effective dopant in reducing the temperature is Tungsten (additional info about tungsten and after that it considers other dopants).

Thinner thickness, stress and strain can also reduce the thermchromic transition temperature.

A little bit on VO_2 thin film durability?
Methods of preparing Pure and doped Vanadium(IV) Oxide Films:
Sol-Gel Method: forming thin films by dip- or spin-coating substrates with solutions of metal alkoxides.
PVD Method: energetically removing atoms/molecules under reduced pressure conditions, then to react with seed gas.
CVD method: chemical vapor deposition, in particular atmospheric pressure CVD (APCVD).
APCVD: deposit tin solid films from gaseous precursors onto a suitable substrate. (+Pictorial representation)
(and more on APCVD).

Comparison of the above methods.

3 atom percent tungsten(VI) $\rightarrow$ transition temperature reduced to 5°C.
1.9 percent $\rightarrow$ 29°C.
transition temperature decreases linearly with tungsten atom percent incorporation(Figure).

Summary: intelligent TC glass with desired switch temperature$(25 - 30^{circ}$C, obtainable using APCVD. Mst of the problems regarding commercial use are solvable. Market in household, offices, factories and space exploration.

[3] **Thermochromism in Commercial Products**

- Thermochromic liquid crystals: Periodicity between layers, PITCH, and constructive interference!. TC liquid crystals can have a versatile range of colors and useful color changes bewteen -30 and 120°C, often with very high temperature sensitivity. TC liquid crystals are only useful when they are in the liquid crystalline phase, which is a meso-phase (an intermediate phase of matter) between an isotropic liquid (high temperature) and crystalline solid (low temperature), which restricts the temperature range of theur applicability.

- **Microencapsulation**: Defined as the coating of small solid particles, liquid droplets, or gas bubbles with a thin film or coating or shell material, and typical particle sizes are 1 to 1000 μm ([20] Kirk-Othmer Encycloped. of chem. Tech. 4thEd). For three component organic mixtures, particle sizes are < 50 μm. **Micro encapsulation allows the additional advantage of combinations of several narrow color ranges**, and very sharp color changes, as well as protection of the coloring agent from the environment ([16] Nakasuji med flere. Chem.Abs.). **complex coacervation** and **interfacial polymerization** $\rightarrow$ processes to microencapsulate thermochromic materials! Also described! Nice to include if I use thin layer on my granular film!

- Smart window candidates: Fe_3O_4, $FeSi_4$, NbO_2, NiS, Ti_2O_3 and VO_2, which owe their temperature change to a semiconductor-to-metallic state transition (aka **Mott transition temperature**)

- Wyszecki and Stiles stated ([2] color science), for TC transmitting filters, that the spectral transmittance curve at a given wavelength with a large positive slope usually dereases with increasing temperature. As a rule: steeper(positive) slope → greater temperature effect!
  The curve with negative slope is of minor importance, but often causes transmittance increase for increasing temperature (if it is important).

  Neutral samples (gray, white, black) did not exhibit TC, because their spectral reflectance curves have a small or no slope.

- Assuming nonfluorescent, linear material which is "nice" with respect to polarization effects, then

$$1 = R_\lambda + A_\lambda + T_\lambda$$

where, R_λ is the reflectance, A_λ is the absorbance and T_λ is the transmittance of the sample.
Considering **transmitting samples**, the intensity I_λ transmitted through a sample of thickness d is given by

$$I_\lambda = I_{0\lambda} e^{-\mu_\lambda d}$$

where μ_λ is the absorption coefficient of the sample at wavelength λ. The optical density D is then given by:

$$D = -\log(T_\lambda) = -\log(\frac{I_\lambda}{I_{0\lambda}}) = \mu_\lambda d \log e = \frac{\mu_\lambda}{\ln 10}$$

For **opaque samples** there is no transmittance, but the optical density can be calculated from the reflected intensity $I_{R\lambda}$:

$$D_\lambda = -\log(\frac{I_{R\lambda}}{I_{0\lambda}}).$$

The light reflected from the material is also exponentially attenuated, for opaque materials. Thus, $D = \frac{\mu_\lambda}{\ln 10}$ holds for reflected light if d is the distance the reflected light has passed in the material.

[**?**] **A Qualitative Description of Thermochromism in Color Measurements**

•

[1] **Performance, materials and coating technologies of thermochromic thin films on smart windows**

- A significant amount of energy is consumed to maintain thermal comfort in buildings, a huge portion which is lost through windows. smart windows obtained by thin films is the solution. The touchstone of performance is the change in visible and infra-red transmission and reflectance!

- A significant amount of the energy consumption in buildings are mainly due to HVAC (heating, ventilation and air conditioning) devices, used to obtain thermal comfort, The building energy consumption in developed contries accounts for 20-40% of the total energy use. (including further details of US and China energy consumption). The building energy consumption is even more dominant in hot and humid regions, using one-third to half of the elextricity produced in some contries. Energy related carbon dioxide emmision. Motivates energy saving measures to reduce building energy losses and CO_2 emissions.

- Two approaches to increase energy efficieny (7-10)
    - Active stratergies: improving HVAC systems and building lighting.
    - Passive stratergies: improving the thermal properties of the building envelope (elementss separating the indoor from outdoor), i.e. thermal insulation to wall, cool coatings on roofs and coated window glazings.

- Windows are known as one of the most energy inefficient components of buildings.(11)
Improving the thermal performance of windows will result in reduced electricity costs and less greenhouse gas emmissions.
In addition to controlling transmitted IR radiation an ideal window should be capable of sufficient transmission of visible light(12).
Improving glazing characteristics of windows such as thermal transmittance and solar parameters is the most important criterion to be considered in building winows standards (14).

- International and local standards related to energy and lighting performance of windows TABLE.

- **Smart windows** defined as the type of windows that partially block the unwanted solar radiation. The energy performance can be improved by increasing heat gain in cold weather and decreasing it in hot weather by adopting windows radiative and thermal properties dynamically (25). Adding a controllable absorbig layer on teh surface of hte glass can change the optical properties of the glass by controlling the incident solar heat flux(26). Therefore, smart windows lead to reduced HVAC.energy consumption, size and elecric demand of the building (11,27,28).

- (Low emissivity (low-E) coatings are spectrally selective films that are aimed to let the visible light pass through and block the IR and UV-wavelengths which generally create heating(10). Typically, there are two types of these coatings: the tin oxide based hard coating and the silver based soft coating with higher IR reflectance and lower transmittance. The visible transmittance of hard coatings can be boosted with anti-reflecting silicon dioxide (29).)

- **The switchable reflective devices** (also called dynamic tintable windows) are categorized into **passive-** and **active systems**:
    - Passive devices: the switching process is activated automatically in accordance with the environmental conditions, e.g. temperature and heat in thermochromic windows.
    - Actice systems: Require an external triggering mechanism to perform the modulation. For instance, electricity is the actuating signal in electrochromic windows. The active switchable glazing systems offer supplementary options compared to the passive systems whereas their dependenvy on power supply and wiring should be reckoned with as a drawback.

- Chromic material, liquid crystals and suspended particle windows are the three most common active controlled intelligent windows (11). (Chromic materials = electrochromic(active), gasochromic(active), photochromic and thermochromic.

- Providing a see-through mode is a must in any application.

- (p.356) The technology using liquid crystals in intelligent windows is called Polymer. Dispersed liquid crystals (PDLC).

- Electrochromic windows and thermochromic windows demand the lowest cooling energy, where the former require less energy for lighting than the latter (69). **Figure 1 (24) (nice figure comparing TC to the other chromic glazings together with clear glass, tinted glass and reflective glass)** .

- **Thermochromic Windows**: **ALSO NOTE PAGE 357! ALOT OF NICE FIGURES!!!**
  Word originates from the Greek roots: "thermos" meaning warm or hot; and "Chroma" which means color. Generally TC materials change color in response to temperature variations.
  The TC thin film is initially in its monoclinic state(cold state) at lower temperatures (usually room temperature). Monoclinic materials behave as semiconductors, less reflective especially in the near-IR (NIR) radiation. As the temperature becomes higher than a certain point, the TC material changes its nature from monoclinic to rutile state(hot state), where the material acts like a semi-metal, reflecting a wide range of solar radiation (76). **FIGURE 3** The transition is called **metal to semiconductor transition (MST)**.

- **Figure 4**, The majority of the heat gain in solar spectrum takes place at NIR range (800-1200 nm) (78-80). The red line(line 1) indicates the transmittance of a perfect TCW in cold state. Visible light should be transmitted and NIR should be reflected. Long wave radiation is also reflected back to indoor. This transmittance approach leads to reduction of solar heat gain and is apt in nearly all climates.
  The blue line(line 2) indicates the tranmittance of a perfect TCW in its hot state. Visible and near infrared radiation are transmitted, while long-wave infrared is reflected to inside. This transmittance mode is suitable in low temperature climates where solar heat gain is desired. Therefore, in high temperatures, TCW reduce NIR and far-IR transmittance, while in low temperatures they allow these parts of solar adiation to pass (82), (Figure 5).
  The MST is fully reversible, co-occurred with large variations in electrical and optical properties in NIR range (83). The MST temperature should decrease to near the ambient temperature. Doping metal ions into the lattice of TC materials can alter the transition temp(84,85). The size and charge (84,86,87) of dopant ion, film's strain (88,89) as well as the variations in electron carrier density are the determinant factors prevailing on the fall or rise of the transition temperature (90).

- The **Ideal spectral behavior of TCW** is presented in **Table 3**. The visible transmission and reflectance should be equal on both sides of transition, while the infra-red variations are from 0% to 65%. The change in transmittance (ΔT%) and reflectance (ΔR%) can be formulated as (92):

$$\Delta T\% = (T_{hot} - T_{cold}) \cdot 100$$
$$\Delta R\% = (R_{hot} - R_{cold}) \cdot 100$$

  where hot and cold denotes transmittance/reflectance at the hot and cold state respectively.

- The most common TC material in TCWs is pure **vanadium dioxide**, with a transition temperature of 68°C which shoud be decreased to ambient temperature for practical use.
  The most critical weakness of VO_2 coatings is their low transmittance in the visible range. Many studies have reported values between 40% and 50%, which is well below the acceptable value of 60% (93, 94). **Table 4** shows the reported values of transmittance and reflectance in the visible and IR range for VO_2.

- Low energy-saving efficiency also limits the application of VO_2 coatings. The change in transmittance before and after the transmittion temperature T_t, at 2500nm, is known as the **switching efficiency** η_T and is the benchmark of energy-saving efficiency. (?why? because of lighting?). This value is inlcuenced by doping(107,108), microstructure(80,95,109-111), **and film thickness (80,88)**. The most paramount factor among them is film thickness that affects the switching efficiency most significantly. However, increasing the film thickness has an adverse effect on T_{vis}. As observed from table 4, **the ideal film thickness is between 40 and 80 nm**.

- Crucial Steps to overcome the limited application of TWCs:

  - Suitable doping(reducing T_t and improving T_{vis})
  - Appropriate Coating Technology
  - Adding efficient anti-reflecting coating(to increase T_{vis}) (read next title in article)
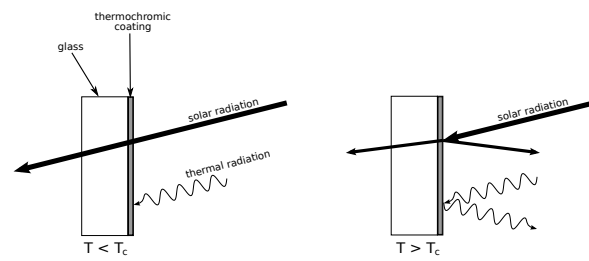 - Reducing coating costs

Figure 6.1: Schematic demonstration of the application of thermochromic materials to advanced window glazing [8]. In the article it is used as a pictorial representation of how vanadium(IV) oxide thin film will work as an intelligent window.

References

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