VO$_2$-based Thermochromic and Nanothermochromic Materials for Energy-Efficient Windows

Computational and Experimental Studies

SHUYI LI
VO₂-based films are thermochromic and exhibit high or low infrared transmittance when the temperature is below or above a critical temperature. The thermochromic switching is passive and reversible, and therefore VO₂-based films are promising for energy-efficient window applications. However, the practical use of VO₂ for energy-efficient windows has long been hampered by low luminous transmittance and low solar energy transmittance modulation. The main goal of this dissertation work is to address these issues.

The first half of the work proposes the concept of nanothermochromics for simultaneous improvement of luminous transmittance and modulation of solar energy throughput. Nanothermochromics considers VO₂ nanoparticle composite layers, whose optical properties were modeled by effective medium theories. Calculations on VO₂ spheroids have shown that VO₂ nanoparticles, especially nanospheres, can offer dramatically improved luminous transmittance and solar transmittance modulation that are not possible for films. Calculations done on core-shell nanoparticles showed comparable improvements and offer an opportunity to reduce the material costs. It was also found that the composite of In₂O₃:Sn (ITO) and VO₂ can yield moderately high luminous transmittance, solar transmittance modulation and low-emittance properties.

In the second half of the dissertation work, Mg-doped VO₂ films were sputter deposited. Their band gaps and Mg-content were investigated by means of optical absorption measurement and Rutherford backscattering spectrometry, respectively. The band gaps of VO₂ were found to increase by ≈3.9±0.5 eV per unit of atom ratio Mg/(Mg+V) for 0<Mg/(Mg+V)<0.21. Computations based on effective medium theory were done to estimate the performance of Mg-doped VO₂ films and nanoparticle composite layers. The results suggest that moderately doped VO₂ films with 0<Mg/(Mg+V)<0.06 perform better than undoped films and that the performance can be further enhanced with one layer of antireflection coating. The best results were achieved by undoped VO₂ nanospheres, closely followed by the VO₂ nanospheres with low Mg-content.

Furthermore, an experimental study on sputter deposited VO₂ nanorods has identified the geometry of the oxygen gas inlet, the type of substrate, the substrate temperature and the layer thickness as important factors that influence the growth morphology.

Taken as a whole, nanothermochromics offered by VO₂ nanoparticles was shown to be the best solution for VO₂-based thermochromic energy-efficient window coatings.

Keywords: VO₂, thermochromism, nanothermochromics, energy efficient windows, optical modeling, effective medium theory, thin film characterization, doping

© Shuyi Li 2013

ISSN 1651-6214
ISBN 978-91-554-8801-7
urn:nbn:se:uu:diva-210016 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-210016)
To my family and friends
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


VI  Shu-Yi Li, Gunnar A. Niklasson, and Claes G. Granqvist, Thermochromic undoped and Mg-doped VO$_2$ thin films and nanoparticles: Optical properties and performance limits for energy efficient windows, *in manuscript*

Reprints were made with permission from the publishers.

Papers not included in the thesis


XI I. Lykissa, S. Li, M. Ramzan, R. Ahuja, C.-G. Granqvist, and G. A. Niklasson, Electronic density of states of amorphous vanadium pentoxide films: Electrochemical measurements and density functional theory calculations, *in manuscript*

Conference papers


Book chapter

My contribution to the appended papers.

I All the modeling and calculation, most of the analysis and part of the writing.
II All the modeling and calculation, most of the analysis and part of the writing.
III All the modeling and calculation, most of the analysis and part of the writing.
IV All the modeling and calculation, most of the experiment analysis and writing.
V All the modeling and calculation, most of the experiment analysis and writing.
VI All the modeling and calculation, most of the experiment analysis and writing.

Disclaimer: Half of this Ph.D thesis is based on my licentiate thesis titled: *VO₂-based Nanothermochromics for Energy Efficient Windows: Calculated results*, which was intended as a half-time report for my Ph.D project.
List of symbols and abbreviations

Greek letters

\( \alpha \)  
Absorption coefficient

\( \alpha_{pol} \)  
Polarizability

\( \Gamma \)  
Damping coefficient in Lorentz model

\( \Delta T_{sol} \)  
Modulation of solar energy throughput, i.e. solar transmittance modulation.

\( \delta \)  
Phase change during the passage of light in the film

\( \varepsilon \)  
Complex dielectric function

\( \varepsilon^A, \varepsilon^B \)  
Dielectric functions of component A and B in Bruggeman theory

\( \varepsilon^{BR} \)  
Effective dielectric function obtained from Bruggeman theory

\( \varepsilon^{eff} \)  
Effective dielectric function

\( \varepsilon^{MG} \)  
Effective dielectric function obtained from Maxwell-Garnett theory

\( \varepsilon_0 \)  
Dielectric permittivity in empty space

\( \varepsilon_1 \)  
Real part of the complex dielectric function

\( \varepsilon_2 \)  
Imaginary part of the complex dielectric function

\( \varepsilon_c \)  
Dielectric function of the particle core

\( \varepsilon_f \)  
Dielectric function obtained from films

\( \varepsilon_m \)  
Dielectric function of the hosting matrix

\( \varepsilon_p \)  
Dielectric function of the particle inclusion

\( \varepsilon_s \)  
Dielectric function of the particle shell
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_\infty$</td>
<td>Dielectric background</td>
</tr>
<tr>
<td>$\varepsilon_f^D, \varepsilon_p^D$</td>
<td>Drude type terms of the dielectric function of films and nanoparticles respectively</td>
</tr>
<tr>
<td>$\varepsilon_{\text{max}}$</td>
<td>Largest of the dielectric functions in a composite material</td>
</tr>
<tr>
<td>$\varepsilon_{\text{sub}}$</td>
<td>Dielectric function of the substrate</td>
</tr>
<tr>
<td>$\varepsilon_{\text{therm}}(\lambda), \varepsilon_{\text{therm}}(T_t)$</td>
<td>Wavelength and temperature-dependent thermal emittance, respectively.</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Angle of incidence</td>
</tr>
<tr>
<td>$\theta_{\text{scatter}}$</td>
<td>the angle between the incident and diffracted beam in XRD.</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>Wavelength where maximum radiated energy occurs</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Frequency of light</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Slope value of linear trend extracted from band gap as a function of Mg/(Mg+V) atom ration $z$ as in Eq. (8.1)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>mass density</td>
</tr>
<tr>
<td>$\rho_R$</td>
<td>Resistivity</td>
</tr>
<tr>
<td>$\sigma_{\text{SB}}$</td>
<td>A constant mentioned in the Stefan-Boltzmann law in Eq. (2.2)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$\tau_{\text{cr}}$</td>
<td>Critical temperature for metal-to-insulator transition in VO$_2$</td>
</tr>
<tr>
<td>$\tau_f$</td>
<td>Mean scattering time for the conduction electrons in thin films (or bulk)</td>
</tr>
<tr>
<td>$\tau_p, \tau_f$</td>
<td>Mean scattering time for the conduction electrons nanoparticles, and thin films (or bulk) respectively.</td>
</tr>
<tr>
<td>$\tau_{\text{sc};n}$</td>
<td>Scattering time, $1/\tau_{\text{sc};n}$ is proportional to the width of each transitions represented by Lotentz oscillator in Eq. (4.18) and (4.19)</td>
</tr>
<tr>
<td>$\tau_{\text{sc}}$</td>
<td>Scattering time</td>
</tr>
</tbody>
</table>
$\varphi_{lum}$  Luminous efficiency of the human eye

$\varphi_{sol}$  Solar irradiance spectrum when the sun is standing 37° above the horizon (corresponds to air mass 1.5 or AM 1.5)

$\Omega$  Volume ratio between the inner and outer spheroids of a core-shell structure

$\omega$  Angular frequency of the electromagnetic wave, i.e. light

$\omega^*$  Screened plasma frequency

$\omega_n$  Characteristic band-to-band transition energies in Eq. (4.18) and (4.19)

$\omega_p$  Plasma frequency

$\omega_0$  Frequency of the restoring force in Lorentz model

$\omega_{pf}, \omega_{pp}$  Plasma frequency for electrons in films and nanoparticles, respectively

$\omega_{res}$  Localized surface plasma resonance frequency for small particles

**Roman letters**

$a$  Major axis of spheroidal particles

$A_n$  Spectral weight of band-to-band transitions in Eq. (4.18) and (4.19)

$A(\lambda)$  Wavelength-dependent absorptance

$A_i$  atom $A_i$

$c$  Minor axis of spheroidal particles

$c_0$  Speed of light

$C_{Wien}$  A constant mentioned in Wien’s displacement law in Eq (2.3)
\( D \)  
Dielectric displacement

\( d \)  
thickness

\( D_p \)  
Particle diameter

\( d_t, d_b \)  
thicknesses of top and bottom layers in the structural models describing nanorod samples mentioned in Section 9.2

\( d_{hkl} \)  
distances between crystall planes \((hkl)\)

\( E \)  
Electromagnetic wave in matter

\( E_0 \)  
Incident electromagnetic wave

\( E_g(0) \)  
band gap for zero Mg content as in Eq. (8.1)

\( E_g(z) \)  
band gap as a function of Mg/(Mg+V) atom ratio \( z \) as in Eq. (8.1)

\( E_F \)  
Fermi level

\( E_{g1}, E_{g2}, E_{g3} \)  
Band gaps for the semiconducting state of VO\(_2\)

\( E_g \)  
Band gap from O 2\( p \) to the Fermi level for the metallic state of VO\(_2\)

\( e_{OS,PS} \)  
A parameter that is a function of principal axes of prolate or oblate spheroids

\( E_{therm} \)  
Total integrated hemispherical thermal emittance

\( f \)  
Filling factor, i.e., the volume fraction occupied by the particles.

\( f_t, f_b \)  
filling factor of VO\(_2\) nanoparticles in top and bottom layers in the structural models describing nanorod samples mentioned in Section 9.2

\( F_{hkl} \)  
Structure factor

\( h \)  
Plank’s constant

\( \bar{h} \)  
Plank’s constant divided by 2\( \pi \)

\( I(\lambda, T_i) \)  
Wavelength-dependent distribution of the radiated energy per unit time per unit volume per unit solid angle per unit wavelength from a black body

\( I_{hkl} \)  
Intensity of Bragg reflection
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{int}$</td>
<td>Radiated power per unit area of the black body</td>
</tr>
<tr>
<td>$k$</td>
<td>Imaginary part of the complex refractive index</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>$\ell$</td>
<td>Electron mean free path in thin films (or bulk)</td>
</tr>
<tr>
<td>$\ell_f$</td>
<td>Electron mean free path in the film</td>
</tr>
<tr>
<td>$L$</td>
<td>Depolarization factor</td>
</tr>
<tr>
<td>$L_{eff,i}, i=1, 2, 3$</td>
<td>The effective depolarization factors of particle aggregates.</td>
</tr>
<tr>
<td>$L_i, i=1, 2, 3$</td>
<td>Depolarization factors along the principal axes of ellipsoids</td>
</tr>
<tr>
<td>$L_{\text{length}}$</td>
<td>The length dimension of sampled area along the flow of current in 4-wire method.</td>
</tr>
<tr>
<td>$L_{\text{width}}$</td>
<td>The width dimension of sampled area perpendicular to the current in 4-wire method.</td>
</tr>
<tr>
<td>$M$</td>
<td>Interface matrix</td>
</tr>
<tr>
<td>$m$</td>
<td>Aspect ratio of spheroidal particles</td>
</tr>
<tr>
<td>$m_e^*$</td>
<td>The effective mass of electron.</td>
</tr>
<tr>
<td>$m_i$</td>
<td>mass of atom $A_i$</td>
</tr>
<tr>
<td>$N$</td>
<td>Complex refractive index</td>
</tr>
<tr>
<td>$n$</td>
<td>Real part of the complex refractive index</td>
</tr>
<tr>
<td>$n_c$</td>
<td>Complex refractive index of the nanoparticle core</td>
</tr>
<tr>
<td>$n_e$</td>
<td>Charge density</td>
</tr>
<tr>
<td>$n_i$</td>
<td>the number fraction of atom $A_i$</td>
</tr>
<tr>
<td>$n_m$</td>
<td>Complex refractive index of the dielectric matrix</td>
</tr>
<tr>
<td>$n_s$</td>
<td>Complex refractive index of the nanoparticle shell</td>
</tr>
<tr>
<td>$n_x$</td>
<td>An integer that represents the order of diffraction</td>
</tr>
<tr>
<td>$N_{\text{area}}$</td>
<td>number of atoms per area as determined by Rutherford backscattering spectrometry</td>
</tr>
<tr>
<td>$p$</td>
<td>Dipole moment</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>r</td>
<td>Displacement in Eq. (4.7)</td>
</tr>
<tr>
<td>$R$</td>
<td>Intensity reflectance</td>
</tr>
<tr>
<td>$R(\lambda)$</td>
<td>Wavelength-dependent reflectance</td>
</tr>
<tr>
<td>$R_{\text{BaSO}_4}$</td>
<td>Reflectance of BaSO$_4$ reference sample.</td>
</tr>
<tr>
<td>$r_{\text{coh}}$</td>
<td>Amplitude reflectance for a coherent layer</td>
</tr>
<tr>
<td>$R_{\text{diff}}$</td>
<td>Diffuse reflectance</td>
</tr>
<tr>
<td>$R_{\text{lum}}$</td>
<td>Luminous reflectance</td>
</tr>
<tr>
<td>$R_{oi}$</td>
<td>Reflectance from outer half space $i$ to inner halfspace $o$</td>
</tr>
<tr>
<td>$R_{\text{res}}$</td>
<td>Resistance</td>
</tr>
<tr>
<td>$R_{s,p}$</td>
<td>Intensity reflectance of s- and p-polarized light</td>
</tr>
<tr>
<td>$r_{s,p}$</td>
<td>Amplitude reflectance of s- and p-polarized light</td>
</tr>
<tr>
<td>$R_{\text{sol}}$</td>
<td>Solar reflectance</td>
</tr>
<tr>
<td>$R_{\text{spec}}$</td>
<td>Specular reflectance</td>
</tr>
<tr>
<td>$R_{\text{tot}}$</td>
<td>Total reflectance</td>
</tr>
<tr>
<td>$S$</td>
<td>Layer matrix</td>
</tr>
<tr>
<td>$S_{1,\text{tot}}, S_{1,\text{diff}}$</td>
<td>The total and diffuse signal recorded using transmittance setting in Lambda 900 instrument, respectively.</td>
</tr>
<tr>
<td>$S_{2,\text{tot}}, S_{2,\text{diff}}$</td>
<td>The total and diffuse signal recorded using reflectance setting in Lambda 900 instrument, respectively.</td>
</tr>
<tr>
<td>$T$</td>
<td>Intensity transmittance</td>
</tr>
<tr>
<td>$t$</td>
<td>The thickness of the particle shell</td>
</tr>
<tr>
<td>$T(\lambda)$</td>
<td>Wavelength-dependent transmittance</td>
</tr>
<tr>
<td>$T_l$</td>
<td>Temperature of the radiating black body</td>
</tr>
<tr>
<td>$t_{\text{coh}}$</td>
<td>Amplitude transmittance for a coherent layer</td>
</tr>
<tr>
<td>$T_{\text{diff}}$</td>
<td>Diffuse transmittance</td>
</tr>
<tr>
<td>$T_{\text{lum}}$</td>
<td>Luminous transmittance</td>
</tr>
<tr>
<td>$T_{oi}$</td>
<td>Transmittance from outer half space $i$ to inner halfspace $o$</td>
</tr>
</tbody>
</table>
\begin{align*}
T_{s,p} & \quad \text{Intensity transmittance of s- and p-polarized light} \\
t_{s,p} & \quad \text{Amplitude transmittance of s- and p-polarized light} \\
T_{sol} & \quad \text{Solar transmittance} \\
T_{spec} & \quad \text{Specular transmittance} \\
T_{tot} & \quad \text{Total transmittance} \\
t_{t} & \quad \text{Time} \\
v_{Ff} & \quad \text{Fermi velocity of electrons in thin films (or bulk)} \\
x & \quad \text{Displacement in Eq. (4.6)} \\
x & \quad \text{The diameter of the particle core} \\
z & \quad \text{Mg/(Mg+V) atom ratio}
\end{align*}

**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR</td>
<td>Antireflection</td>
</tr>
<tr>
<td>at.%</td>
<td>Atomic percent</td>
</tr>
<tr>
<td>EC</td>
<td>Electrochromic</td>
</tr>
<tr>
<td>GIXRD</td>
<td>Grazing incidence X-ray diffraction</td>
</tr>
<tr>
<td>low-E</td>
<td>Low thermal emittance</td>
</tr>
<tr>
<td>NIR</td>
<td>Near infrared</td>
</tr>
<tr>
<td>OS</td>
<td>Oblate spheroids</td>
</tr>
<tr>
<td>PS</td>
<td>Prolate spheroids</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford backscattering spectrometry</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
<tr>
<td>vol.%</td>
<td>Volume percent</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
Part I:
Basics
1. Introduction

The industrial revolution has to a great extent raised the material aspects of life in developed countries as well as in prosperous cities in developing countries: people have abundant food, enjoy the comfort and convenience that a king would have envied 200 years ago [1], have the means to travel half way around the globe within a day and access a lot of information with a few clicks. The world is getting smaller and is looking increasingly finite, thanks to the immense processing power of industry for turning energy and resource into end products; perhaps too hastily and recklessly. Many have come to realize that old sources of energy and resources are getting less available, while, the problem of environmental pollution is deepening.

Most energy-related issues can be included in the following three genres: i) generation; ii) storage; iii) distribution and iv) efficiency, -"to manage a little well". i), ii) and iii) points to the new technologies to unlock the potential of renewable energies and produce novel batteries and smart power system networks. iv) however, has existed throughout human history. The ancient Chinese people had an efficient way of cultivating rice and fish together so that no feeding or fertilizing was needed. The quote "to manage a little well" is from Isabella Beeton’s masterpiece [2], wherein she documented the system of keeping up a Victorian well-to-do lifestyle while making sure that every bit of material was put to good use and nothing was lost or wasted. I would like to take this quote as an interpretation of "energy-efficiency" as it does not mean diminishing one’s necessities or even comforts, but cutting back on avoidable waste and loss by solving a series of design problems. This thesis deals with energy-efficiency of a fundamental building component, i.e., windows.

Buildings (i.e., the dwellings of modern humans) are among the major energy consumers and have a large environmental impact. Around 30-40 % of world primary energy consumption is due to heating, cooling, ventilation, lighting and appliances in buildings [3]. In the industrialized world, these figures tend to be larger. Buildings account for 39% of energy consumption in the USA [4] (year 2008) and 40-45% in Europe [3] (year 2007). The good news is the potential for energy saving in buildings is also large, if smart energy-efficient technologies and designs are utilized [4].

Windows are a necessity for buildings for providing lighting and visual contact with the outside world, and they are becoming a larger and larger presence in modern architecture. However, in terms of energy efficiency, they are a weak link due to the fact that windows very often let in or let out too much
energy, and adds to energy consumption especially in summer and winter. Therefore, windows, as they have a big impact on energy consumption/saving, need to be made energy-efficient.

There are many ways to control the energy throughput and daylighting properties of windows. Low-emittance (low-E) windows and solar control windows are the typical energy efficient windows for passive control of indoor heat loss and solar energy throughput, respectively. These types of window constantly transmit a part of the light spectrum and block the rest. They have very low thermal emittance and are capable of achieving good heat insulation while maintaining high transparency in the visible. They are already widely in use in many developed countries. Photochromic, thermochromic, electrochromic, and gasochromic materials belong to a class of materials known as chromogenic materials[5]. Chromogenic materials are "smart" and switchable, and therefore offer better options for energy-efficient fenestration. By combining several chromogenic materials, one can work toward "super fenestration" [6, 7].

The focus of this thesis is on VO$_2$-based thermochromic materials. VO$_2$ has a switchable infrared optical property when the temperature is changed across a critical temperature $\tau_{cr}$. It has a great potential for energy efficient fenestration [8–12], especially in hot climates [12]. The issues that have hindered the practical applications of VO$_2$ in windows are the low luminous transmittance and modest solar transmittance modulation. In works covered by this thesis, a proposal for nanothermochromics is made based on computation results which showed that VO$_2$-based nanoparticles can have very much improved luminous properties and solar modulation (Chapter 7). The thesis also contains experimental studies on Mg-doped VO$_2$ films that have revealed a well-defined trend between the visible optical band gap of the films and the Mg content (Section 8.1). The followup computational studies (Sections 8.2, 8.3) show that the moderately Mg-doped films outperform the undoped VO$_2$ films, and better performances can be achieved by one layer of antireflection coating, but the best performance is still offered by VO$_2$ nanoparticles. As a side project, the growth of sputter deposited VO$_2$ nanorods was investigated and the findings are presented in Chapter 9.
2. Energy Efficient Windows

2.1 The Solar Spectrum and Window Performance

2.1.1 Black Body Radiation and the Solar Spectrum

A black body by definition is something that absorbs all the incident electromagnetic radiation, i.e., \( A(\lambda) = 1 \). Black bodies with a temperature of above absolute zero degrees radiate thermal energy in the form of electromagnetic waves. The wavelength-dependent distribution of the radiated energy per unit time per unit volume per unit solid angle per unit wavelength \( I(\lambda, T_t) \) is described by Plank’s law:

\[
I(\lambda, T_t) = \frac{8\pi\hbar c_0}{\lambda^5} \frac{1}{\exp\left(\frac{\hbar c_0}{\lambda k_B T_t}\right) - 1} 
\]

(2.1)

where \( c_0, h, k_B, \lambda, T_t \) refer to the speed of light, Plank’s constant, Boltzmann’s constant, wavelength and temperature of the radiating black body, respectively. A Figure of Plank’s law for different temperatures is shown in Fig 2.1 (a).

Integrating Eq. (2.1) over wavelength and solid angle over a half sphere, we have the Stefan-Boltzmann law, which gives radiated power per unit area of the black body \( I_{int} \):

\[
I_{int} = \sigma_{SB} T_t^4 
\]

(2.2)

where \( \sigma_t = 5.6705 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4} \). Another important relation, Wien’s displacement law, states the relation between the wavelength where the maximum radiated energy occurs \( \lambda_{max} \) and the temperature of the radiating black body \( T_t \):

\[
\lambda_{max} T_t = C_{Wien} 
\]

(2.3)

with \( C_{Wien} = 2.8978 \times 10^{-3} \text{m K} \).

The Stefan-Boltzmann law and Wien’s displacement law allow us to qualitatively estimate that the higher the temperature of the black body, the more energy it radiates, and at the shorter wavelength this energy peaks.
Figure 2.1: Black body radiation at different temperatures (a) and luminous efficiency of the human eye [13] together with solar irradiance spectra that travels through the atmosphere [14] (b) plotted in the same wavelength scale. Note that in (a) the spectral intensities have comparable scales apart from the one with "5505 °C", which is drawn for convenience.

The sun is a blackbody. The very brightness of the sun is nothing but the black body radiation. The surface temperature 5778 K (5505 °C) of the sun corresponds to the black body radiation at 5505 °C, as shown in Fig. 2.1 (a). It gets partially consumed by absorptions on its path etc. and reaches the earth as a not so perfect bell-shaped spectrum, illustrated in Fig. 2.1(b) and available at our windows on a sunny day. It is important to note that solar energy is only limited to $0.25 < \lambda < 3 \, \mu m$, which does not overlap with thermal radiation from objects at $< 100^\circ$C. Therefore it is possible to devise materials with different properties regarding solar radiation and thermal radiation from the indoor environment.

Solar energy is divided into 3 intervals: $\lambda < 0.4 \, \mu m$ is the ultra-violet (UV) which contributes to vitamin D formation or causes skin damage. $\lambda > 0.7 \, \mu m$ is the near infrared (NIR) which contributes to solar heat, and the interval in between, $0.4 < \lambda < 0.7 \, \mu m$ is the visible range where the sensitivity of the human eyes spans with a peak at 0.555 \,\mu m, as shown in Fig. 2.1(b).
2.1.2 Basic Light-matter Interaction

When placed in an incident light beam, a material can respond in three ways, it can transmit, reflect or absorb the electromagnetic energy. These processes must obey the energy conservation law at each wavelength:

\[ T(\lambda) + R(\lambda) + A(\lambda) = 1 \quad (2.4) \]

where, \( \lambda \) is the wavelength and \( T(\lambda), R(\lambda), A(\lambda) \) refer to the wavelength-dependent transmittance, reflectance, and absorptance, respectively. Part of the absorbed energy will heat up the material and give rise to an emittance. For energy conservation Kirchhoff’s law gives:

\[ A(\lambda) = \varepsilon_{\text{therm}}(\lambda) \quad (2.5) \]

where \( \varepsilon_{\text{therm}}(\lambda) \) is the wavelength-dependent thermal emittance, which is defined as the fraction of the blackbody radiation released at a certain temperature and wavelength. The temperature-dependent total hemispherical emittance \( E_{\text{therm}} \) per unit area of sample surface is then given by:

\[ E_{\text{therm}}(T_t) = \int_0^\infty A(\lambda) I(\lambda, T_t) d\lambda / I_{\text{int}} \quad (2.6) \]

2.1.3 Evaluation of Window Performance

The primary functions of architectural windows are visual contact through the window, day-lighting and some degree of heat control. These functions are achieved by letting through or blocking parts of the solar and infrared spectra. The wavelength-integrated properties at an angle of incidence \( \theta \), luminous transmittance \( T_{\text{lum}} \) and reflectance \( R_{\text{lum}} \), solar transmittance \( T_{\text{sol}} \) and reflectance \( R_{\text{sol}} \), are some of the important factors used to characterize a window. They are defined as:

\[ T_{\text{lum,sol}}(\theta) = \int d\lambda T(\lambda, \theta) q_{\text{lum,sol}}(\lambda) / \int d\lambda q_{\text{lum,sol}}(\lambda) \quad (2.7) \]

\[ R_{\text{lum,sol}}(\theta) = \int d\lambda R(\lambda, \theta) q_{\text{lum,sol}}(\lambda) / \int d\lambda q_{\text{lum,sol}}(\lambda) \quad (2.8) \]

where \( q_{\text{lum}} \) is the luminous efficiency of the human eye, and \( q_{\text{sol}} \) is the solar irradiance spectrum when the sun is standing 37° above the horizon (corresponds to air mass 1.5 or AM 1.5). The spectra of \( q_{\text{lum}} \) and \( q_{\text{sol}} \) are illustrated in Fig. 2.1.

These wavelength-integrated properties allow us to condense the information from complex spectra into easily comparable numbers and hence are
frequently used in academia and industry for performance evaluations, especially, for windows with near-neutral colors. For colored windows, more measures are needed to take into account the visual comfort of users.

For practical windows, it is often important to limit a certain wavelength range in the near-infrared (NIR) or infrared region (IR) while keeping good daylighting and see-through properties in order to achieve energy efficiency. This can be easily achieved due to the fact that the human eye is not sensitive outside the interval $0.4 < \lambda < 0.7 \, \mu m$ and it is blind in $\lambda > 0.78 \, \mu m$, as shown in Fig. 2.1. By blocking part or all of the spectrum within $0.7 < \lambda < 50 \, \mu m$ while keeping high transparency in $0.4 < \lambda < 0.7 \, \mu m$ (i.e. high $T_{\text{lum}}$), the indoor heat loss or solar heat gain can be largely reduced on a window with good see-through properties. Such spectral selectivity is introduced to windows by coatings, usually on the surfaces facing the confined air (or gas, or vacuum) spaces of multiply-glazed windows. In Sections 2.2 and 2.3, I introduce some of the typical window coatings for energy efficiency.

2.2 Low-E and Solar Control Windows

Low-emittance (Low-E) coatings and solar control coatings and are the two most widely used window coatings for controlling solar heat gain. An idealized definition gives:

\[
\text{low-E } \begin{cases} 
T(\lambda) = 1 & \text{for } 0.4 < \lambda < 3 \, \mu m \\
R(\lambda) = 1 & \text{for } 3 < \lambda < 50 \, \mu m 
\end{cases} \\
\text{solar control } \begin{cases} 
T(\lambda) = 1 & \text{for } 0.4 < \lambda < 0.7 \, \mu m \\
R(\lambda) = 1 & \text{for } 0.7 < \lambda < 50 \, \mu m 
\end{cases}
\]

Low-E coatings are common in colder high latitude regions where people like to keep warm inside by letting in the solar heat, while stopping the indoor heat from escaping through the window to the outside. Low-E coatings are typically installed on the surface of the inner pane facing the confined space of a multiple glazed window. Solar control coatings, on the other hand, are designed for warmer regions, where maximum blocking of solar heat is desirable. Solar control coatings are typically installed on the surface of the outer pane facing the confined space of a multiply glazed window.

These coatings are usually based on transparent conducting oxides (TCO) such as tin-doped indium oxide (known as ITO or indium tin oxide and denoted as $\text{In}_2\text{O}_3$:$\text{Sn}$), fluorine-doped tin oxide (FTO, $\text{SnO}_2$:$\text{F}$), aluminium-doped zink oxide (AZO, $\text{ZnO}_2$:$\text{Al}$) or multilayer sandwich structures comprising dielectric layers and thin layers of noble metals [15].
Solar control coatings and low-E coatings highly reflect the thermal infrared and have a low total integrated hemispherical thermal emittance $E_{\text{therm}}$. An uncoated glass is strongly absorbing in the thermal infrared $\lambda > 3 \ \mu\text{m}$ and has an $E_{\text{therm}}$ as large as 0.87. When coated with solar control or low-E coatings, $E_{\text{therm}}$ of the coated glass can be significantly reduced to only a fraction of $E_{\text{therm}}$ of the uncoated glass. $E_{\text{therm}}$ as low as $\sim 0.2$ with $75\% < T_{\text{lum}} < 80\%$ is achievable by using coatings based on TCO [15, 16]. An even lower $E_{\text{therm}} \ll 0.2$ can be achieved by using thin layers of Ag. [11]

2.3 Chromogenic Smart Switchable Windows

Smart switchable windows are another class of energy efficient windows. Instead of offering a static optical control, as solar control and low-E windows do, smart switchable windows have variable optical properties. These can be based on polymer liquid crystal devices, suspended particle devices and chromogenic materials. Here I only talk about chromogenic materials.

Chromogenic materials exhibit a color change triggered by external stimuli. They are called electrochromic (e.g. WO$_3$) if the external stimulus is electrical current or voltage, thermochromic (e.g. VO$_2$) if the stimulus is temperature, photochromic (e.g. some sunglasses) if the stimulus is energetic light, gasochromic (e.g. some Mg alloys) if the stimulus is adsorbed gases.

![Illustration of basic design of an electrochromic (EC) device](image)

*Figure 2.2:* Illustration of basic design of an electrochromic (EC) device, taken from [15].

Electrochromic (EC) devices comprise 5 layers, as illustrated in Fig. 2.2, and switch color when ions are moved by the external electric field in or out
of the electrochromic film. The electric power is only needed for the switching, and the after-switch color of the device can be kept for days at least without any power supply. Among all the chromogenic materials, electrochromic materials are the most studied and some prototypes are already used in commercial products such as windows for buildings, motor cycle helmets, spacecraft etc. [17]. Especially, electrochromic windows, whose optical properties are switchable when a voltage/current is applied, can give the highest energy saving, which can be as high as 4.5% on the annual energy use in the USA when they are installed in commercial and residential buildings [18].

In this thesis I discuss thermochromic materials, which can be as simple as a single layer structure with switchable optical properties depending on temperature. Thermochromic materials by themselves cannot save as much energy as electrochromic materials, but their sheer simplicity makes them easy to combine with other energy-efficient functional windows to achieve "super fenestration" [6, 7].

Many oxides such as NbO₂, FeSiO₂, VO₂, Ti₂O₃, V₂O₃ etc. exhibit thermochromism [11]. Among them, VO₂-based materials are the most interesting. VO₂ changes from infrared transmitting to infrared reflecting when it is heated across a critical temperature \( T_{cr} \approx 68 \degree C \). In the next chapter I explain in detail the switching mechanism, optical properties and challenges of thermochromic VO₂ for energy efficient applications.
3. VO$_2$-based Thermochromism

It is well-known that VO$_2$ undergoes a reversible metal-to-insulator structural transition at a critical temperature $\tau_{cr} \sim 68$ C$^\circ$ in the bulk. At $\tau > \tau_{cr}$ VO$_2$ is tetragonal metallic and infrared reflecting; at $\tau < \tau_{cr}$, it is monoclinic insulating and infrared transparent. This phenomenon, namely thermochromism in VO$_2$ was first discovered by Morin [19]. To take advantage of interesting functions due to temperature-dependent switching, VO$_2$ has been used in various applications for sensing, and in optical communication such as in IR-bolometers, photonic crystals etc., and its application as a passive switchable window glazing for energy efficient applications has also been discussed for decades [9, 15].

In this chapter I look into the band structure of VO$_2$, and discuss the advantages and problems of conventional VO$_2$-based films for energy efficient window applications. Finally I address the great opportunities that VO$_2$ nanoparticles can offer.

3.1 Band structure of VO$_2$

VO$_2$ undergoes a first-order metal-to-insulator transition when the temperature is altered across $\tau_{cr}$. The high temperature metallic state ($\tau > \tau_{cr}$) is tetragonal. This transition was recently shown to be of Mott-Hubbard type [20, 21]. The structural transition of VO$_2$ is of great interest in the field of correlated electron systems. However, rigorous discussions on this subject lie out of the scope of this work, and therefore we will not attempt to go any further than briefly introduce the band structure of VO$_2$.

Fig. 3.1 shows the schematic band structure based on work by Goodenough [22]. For the metallic state of VO$_2$ corresponding to $\tau > \tau_{cr}$ (3.1 (a)), the crystal structure is tetragonal with space group $P4_2/mnm$. Under the influence of the crystal field, the V 3$d$ $t_{2g}$ band splits into $d_{||}$ and $\pi^*$ sub-bands. The hybridization of the V $\pi^*$ band and the O 2$p\pi$ band causes the $\pi^*$ band to be moved upwards, whereas the weak hybridization between the V $d_{||}$ band and the O 2$p$ band leaves $d_{||}$ at the lowest level of all V 3$d$ bands. The metallic behavior is caused by the partially filled $d_{||}$ and $\pi^*$ band. The gap between O 2$p$ and the Fermi level $E_F$ is the band gap $E_g$, corresponding to an optical gap with higher energy.
Figure 3.1: Schematic illustration of the band structure of VO$_2$ based on the seminal work by Goodenough [22]. (a) corresponds to tetragonal metallic state ($\tau > \tau_{cr}$); (b) corresponds to the monoclinic semiconducting state ($\tau < \tau_{cr}$).

For the semiconducting state of VO$_2$ ($\tau < \tau_{cr}$), V atoms dimerize and twist in a zig-zag way along the c-axis, causing the otherwise tetragonal lattice to distort into a monoclinic lattice with space group $P2_1/c$. The $d||$ band splits into two sub-bands, the upper $d||$ band and the lower $d||$ band. The lower $d||$ band is completely filled leaving the $\pi^*$ band completely empty. $E_{g1}$ denotes the energy gap between lower $d||$ and $\pi^*$, $E_{g2}$ denotes the gap between O 2$p$ and $\pi^*$, $E_{g3}$ denotes the gap between lower $d||$ and upper $d||$.

Various studies based on photoemission spectroscopy (PES) [23–27], X-ray absorption spectroscopy (XAS) [25, 27], ultra-violet reflection [23], electron energy loss spectroscopy (EELS) [28], optical measurements [29–31], as well as density functional theory (DFT)-based theoretical studies such as local density approximation (LDA) [32] and generalized gradient approximations (GGA) [33] have been done to determine the energy gaps in the VO$_2$ band structure. In general, for the semiconducting state, the optical transition at $\sim 0.6$ eV is attributed to $E_{g1}$; transitions above 1eV can be attributed to $E_{g2}$ and $E_{g3}$.

### 3.2 VO$_2$ based Thermochromic Windows

#### 3.2.1 Spectral and Wavelength-Integrated Optical Properties

Fig. 3.2(a) and (b) show typical spectral reflectance $R(\lambda)$ and transmittance $T(\lambda)$ expected from a 50 nm thick VO$_2$ film backed by a glass substrate. Strong optical absorption is present in both states in the UV and in a part of the visible, due to the interband transition across the larger gaps, as illustrated in Fig. 3.1. At semiconducting state, $T(\lambda) \sim 40\%$ where the relative lumi-
nous efficiency of the eye has a peak. This increases with the wavelength and reaches $T(\lambda) \sim 75\%-80\%$ at 2500 nm. For the metallic state, $T(\lambda)$ is almost the same as that of the semiconducting state in the range where the eye is most sensitive, whereas, after a broad maximum around 700-800 nm, $T(\lambda)$ decreases progressively at longer wavelengths and reaches $T(\lambda) \sim 20\%$ at 2500 nm. Meanwhile, $R(\lambda)$ for the metallic state increases with wavelength for $\lambda > 1000$ nm and reaches $R(\lambda) \sim 40\%$ at 2500 nm. Comparing the optical data for the semiconducting state and the metallic state, it can be seen that thermochromic switching is clearly present. The most efficient switching in both $R(\lambda)$ and $T(\lambda)$ occurs at $\lambda \sim 2500$ nm.

![Figure 3.2: Typical spectral reflectance (a) and transmittance (b) of a 50 nm thick VO$_2$ film on a glass substrate in semiconducting state ($\tau < \tau_{cr}$) and metallic state ($\tau > \tau_{cr}$) as can be found in work by Mlyuka [34], plotted together with the solar irradiance spectrum and the spectral luminous efficiency of the eye (c). Note that the same data as in (c) was given in Fig. 2.1 (b).](image-url)
The definitions of wavelength-integrated optical properties introduced in Eq. (2.7) gives $T_{lum}(\tau < \tau_{cr}) \approx T_{lum}(\tau > \tau_{cr}) \approx 37.4\%$, and $T_{sol}(\tau < \tau_{cr}) \approx 42\%$ and $T_{sol}(\tau > \tau_{cr}) \approx 35.5\%$. Here we introduce solar transmittance modulation $\Delta T_{sol}$, which is frequently used to evaluate the thermochromic switching performance of VO$_2$ films. It is defined by:

$$
\Delta T_{sol} = T_{sol}(\tau < \tau_{cr}) - T_{sol}(\tau > \tau_{cr})
$$

(3.1)

Eq. (3.1) gives $\Delta T_{sol} \approx 6.5\%$ for the optical data in Fig.3.2.

Typically for conventional VO$_2$ single layer films, one has $T_{lum} \sim 50\%$ and $\Delta T_{sol} \sim 5\%$. The relatively small solar transmittance modulation $\Delta T_{sol}$ stems from the fact that thermochromic switching is most effective at long wavelengths where the solar irradiance intensity is low. If one requires $\Delta T_{sol} \sim 10\%$, it would limit $T_{lum}$ to less than 40\%, which is too low for practical application. Apart from low $\Delta T_{sol}$ and $T_{lum}$, the critical temperature is too high, $\tau_{cr} \sim 68^\circ C$. These challenges need to be effectively addressed in order to achieve practical window applications with VO$_2$-based films. Sections 3.2.2 and 3.2.3 are devoted to these issues.

### 3.2.2 Doping and Multilayer Films

The critical temperature can be influenced by doping. Studies have shown that doping with W, Mo, Ta, Nb and Eu can decrease $\tau_{cr}$, while doping with Ge, Al and Ga will increase $\tau_{cr}$ [22]. In particular, a few percent of W doping can decrease $\tau_{cr}$ to around room temperature [35–38]. However, $T_{lum}$ is still low in this case. Studies on other dopants have been done as well. F-doping was shown to decrease $\tau_{cr}$ [39, 40], and significantly increase $T_{lum}$[41] with somewhat less pronounced switching [41].

A recent study done in our group by Mlyuka et al. showed that Mg-doping can jointly enhance $T_{lum}$ and reduce $\tau_{cr}$ [36]. A band gap widening effect of Mg-doping was also observed [6, 42, 43], in which Mg-doping was found to increase the larger optical gap while leaving the small gap $E_{g1}$ almost unchanged. A theoretical study based on density functional theories [44] have confirmed that Mg-doping causes a lowering of optical absorption in the visible range. This effect is responsible for the increased $T_{lum}$ in Mg-doped VO$_2$ films.

Straight forward optical designs such as multilayer antireflection coatings have been devised to increase $T_{lum}$ and $\Delta T_{sol}$, such as TiO$_2$/VO$_2$ [45], TiO$_2$/VO$_2$/TiO$_2$ [46], SiO$_x$/VO$_2$/SiO$_x$ [47], and TiO$_2$/VO$_2$/TiO$_2$/VO$_2$/TiO$_2$ [34, 48]. The best of them exhibit $\Delta T_{sol} \sim 12\%$, $T_{lum} \sim 45\%$ [34, 48], or $\Delta T_{sol} \sim 15.1\%$, $T_{lum}(\tau < \tau_{cr}) \sim 49.5\%$, $T_{lum}(\tau > \tau_{cr}) \sim 44.8\%$ at normal incidence [45]. A survey of the performances of VO$_2$ films with AR treatments can be found in the literature [49].
To summarize the above, a smart choice of dopants can decrease $\tau_{cr}$ to room temperature, and therefore $\tau_{cr}$ is not a pressing issue any longer. However, the joint improvement of $T_{lum}$ and $T_{sol}$ is only marginal, despite all the scientific effort described above. For this reason VO$_2$ is not yet ready for practical energy efficient window applications, and we need something new to tackle this problem.

3.2.3 Nanothermochromics

VO$_2$ nanoparticles of various shapes have been successfully fabricated by various physical and chemical methods and thermochromic switching has been demonstrated as mentioned in Refs [50, 51] and references therein. There has been a lot of interest in extracting novel properties that are non-existent in the film or the bulk from nanoparticles [52, 53]. Hence, it is only natural to expect new optical properties from materials based on VO$_2$ nanoparticles.

In 2010 a new idea, namely nanothermochromics was proposed in work [50] covered by this thesis. Nanothermochromics considers dilute suspension of VO$_2$ nanoparticles embedded in a dielectric medium. This structure has two advantages that are well-suited to treating the deficiencies of conventional VO$_2$ films:

- Dilute suspensions of VO$_2$ nanoparticles with little scattering can improve $T_{lum}$ in the nanocomposite layer.
- By taking advantage of a tunable localized plasmon resonance in metallic state VO$_2$ nanoparticles, the optical absorption at $\tau > \tau_{cr}$ can be shifted to a shorter wavelength in the near infra-red range where the solar intensity is high, thereby improving the modulation of solar transmittance throughput $\Delta T_{sol}$.

The computational study covered in this thesis shows that nanothermochromics works very well indeed, and the luminous transmittance and solar transmittance modulation can be significantly improved. As is shown later in Chapter 7.1, nanocomposite layers with VO$_2$ solid nanospheres yield a spectral transmittance as shown in Fig. 3.3, with the above-mentioned advantageous features specific for VO$_2$ nanoparticle based layers: $T_{lum}$ is decidedly higher, and a strong absorption band in the metallic state is located around 1.2 $\mu$m, giving rise to a much larger solar transmittance modulation $\Delta T_{sol}$ compared to data of films in Fig. 3.2. Moreover, results in Chapter 7.2 show that VO$_2$ hollow spheres will improve $\Delta T_{sol}$ even more. Another advantage of VO$_2$ nanoparticles is that by embedding them in other functional layers, one can achieve multifunctional coatings. In Chapter 7.3, a computation considers a mixture of VO$_2$ and ITO and yields a thermochromic low-emittance coating with moderately high $T_{lum}$, large $\Delta T_{sol}$ and low $E_{therm}$.

The above mentioned promises can become reality only if the fabrication of VO$_2$ nanoparticles is possible. It is well-known that VO$_2$ with intermediate valence V$^{4+}$ is very difficult to fabricate, the nanoparticle form even more so.
Despite the difficulties, many experimental works have demonstrated successful fabrication of VO$_2$ particles.  

First of all, nanoparticles of VO$_2$ embedded in a silica matrix have been fabricated using hydrogen-aided reduction of a glass containing V$_2$O$_5$ [54, 55], and ion implantation of V and O ions in a silica host [56, 57] and sol-gel deposition [58]. VO$_2$ particles with near-symmetric shapes have been made by wet chemistry [59–66], molten salt synthesis [67], thermolysis [68], pyrolysis [69], confined-space combustion[70], and pulsed laser deposition[71–73]. Doped particles of VO$_2$ [61, 64, 68, 74, 75] and VO$_2$:W deposited on SiO$_2$ nanoparticles[76], VO$_2$ nanorods [77] W-doped VO$_2$ nanowires [78] and VO$_2$ nanosheets [79, 80] have been prepared by wet chemistry.  

Core-shell particles have also been extensively demonstrated by experiments too. Hollow nanospheres and microspheres of VO$_2$ have been made by chemical synthesis[81], and hollow rodlike VO$_2$ by gas-phase synthesis[82]. Transparent polymers with inclusions of VO$_2$ coated SiO$_2$ nanoparticles and
similar composites have been made[83]. SiO$_2$ coated with VO$_2$:W have also been produced too [84]. VO$_2$ shells on SiO$_2$ have been prepared by pulsed laser deposition [85] and VO$_2$ shells on carbon microspheres by means of chemical methods [86, 87]. VO$_2$ inverse opal and nanoscrolls have also been demonstrated.

Recently, the interest in synthesizing VO$_2$ nanoparticle composites is booming due to the advantageous properties for energy-efficient window coatings. VO$_2$-ITO composite films [88]. W-doped VO$_2$ and polysiloxane composites [89]. VO$_2$ and ZrV$_2$O$_7$ composites [90]. VO$_2$ nanoparticle-assembled nanocomposite films [91] were demonstrated. Furthermore, Incorporation of VO$_2$ [92], SiO$_2$/VO$_2$ core/shell structures [93], VO$_2$-Sb:SnO$_2$ composites [94], Mg-doped VO$_2$ nanoparticles [42] into flexible foils have been realized too.

To summarize, VO$_2$-based Nanothermochromics for energy-efficient windows is not only theoretically well-established but also becoming increasingly easier to realize. Windows equipped with high-performance VO$_2$ based thermochromic components are very likely to finally find their way to our homes in the near future.
4. Optics

4.1 Optical Response in Materials

4.1.1 The Complex Optical Constants

A material’s interaction with light can be roughly divided into two kinds, refraction and extinction. The refraction process, on the one hand, involves a change of the wavelength, speed and direction of light passing through a material while preserving the frequency (i.e. energy) of the incident light. The extinction process consisting of scattering and absorption, which on the other hand, removes energy from light and causes attenuation of the incident light amplitude along the path.

Complex optical constants are suitable for describing both refraction and extinction. There are two sets of most commonly used complex optical constants: the complex refractive index $N$ and the complex dielectric constant $\varepsilon$; both are wavelength-dependent. They are inter-related by the simple expression:

$$\varepsilon = N^2$$  \hspace{1cm} (4.1)

with

$$N = n + ik$$  \hspace{1cm} (4.2)

and

$$\varepsilon = \varepsilon_1 + i\varepsilon_2$$  \hspace{1cm} (4.3)

Hence another relation:

$$\varepsilon_1 = n^2 - k^2$$  
$$\varepsilon_2 = 2nk$$  \hspace{1cm} (4.4)

with the inverse relation:

$$n = \left[ \frac{1}{2} \left( (\varepsilon_1^2 + \varepsilon_2^2)^{1/2} + \varepsilon_1 \right) \right]^{1/2}$$

$$k = \left[ \frac{1}{2} \left( (\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1 \right) \right]^{1/2}$$  \hspace{1cm} (4.5)
The complex refractive index comes from the solution of the wave equation based on the Maxwell equation. This solution describes propagating electromagnetic wave in matter, by

\[ E = E_0 \exp \left[ i\omega \left( \frac{N x}{c_0} - t_t \right) \right] \]  \hspace{1cm} (4.6)

where \( E_0 \) and \( E \) are the amplitudes of the incident electromagnetic wave and the electromagnetic wave in matter, respectively. \( \omega \) denotes the frequency of the electromagnetic wave, \( t_t \) denotes time, and \( x \) is the position vector. The propagating electromagnetic wave is influenced by the matter via the complex refractive index: \( n \) changes the phase velocity, and \( k \) attenuates the amplitude along the light path. The intensity \( EE^* \) contains an exponential attenuation factor \( \exp(-2k\omega x/c) = \exp(-4\pi kx/\lambda) \). Factor \( 4\pi k/\lambda \) is called the absorption coefficient, commonly denoted \( \alpha \).

The complex dielectric constant is more meaningful from a microscopic viewpoint. Contributions due to optical response from different microscopic elements are additive. Such contributions are: dipolar arising from the permanent dipoles; ionic due to displacement of charged ions with respect to other ions; electronic due to displacement of electrons with respect to ion cores and the inter-band transition of valence electrons. These microscopic responses are nothing but the oscillation of charges under the force generated by the external electromagnetic field, i.e. light, and can be represented as oscillators. In 4.1.2 and 4.1.3, I introduce two basic oscillator models, the Lorentz model and the Drude model.

4.1.2 The Lorentz Model: Oscillator Model for Bound Charges

The Lorentz Oscillator is a model developed for the description of bound charges. Here, for convenience, we consider the case that these charges are electrons. The model is analogous to that of harmonic oscillators: the external electromagnetic force \(-eE(\omega)\) is the force responsible for acceleration of the electrons; the assumption also includes a restoring force \( m_e^* \omega_0^2 r \) that the electrons are bounded with, and a "friction" \( m_e^* \Gamma dr/dt \) with a damping effect on the oscillator. The equation representing the balance of the forces is given by

\[ -eE(\omega) = m_e^* \frac{d^2 r}{dt^2} + m_e^* \Gamma \frac{dr}{dt} + m_e^* \omega_0^2 r \]  \hspace{1cm} (4.7)

where \( r \) and \( m_e^* \) are the displacement and the effective mass of the electrons, respectively. By putting \( E(\omega) = E_{00}e^{-i\omega t} \) and \( r = r_{00}e^{-i\omega t} \), the solution gives:
The displacement of charged particles gives rise to an induced dipole moment

\[ p(\omega) = -er = \frac{e^2 E}{m_e^* (\omega_0^2 - \omega^2) - i\omega\Gamma} \]  

(4.9)

Summing up the dipoles and assuming a charge density \( n_e \), we have the macroscopic polarization

\[ P(\omega) = n_e p = \frac{n_e e^2 E}{m_e^* (\omega_0^2 - \omega^2) - i\omega\Gamma} \]  

(4.10)

By using the expression for dielectric displacement

\[ D = \varepsilon_0\varepsilon E = \varepsilon_0 E + P \]  

(4.11)

with \( D \) denoting the dielectric displacement and \( \varepsilon_0 \) denoting the dielectric permittivity in empty space, we obtain the complex dielectric constant

\[ \varepsilon(\omega) = 1 + \frac{\omega_p^2}{(\omega_0^2 - \omega^2) - i\omega\Gamma} \]  

(4.12)

where the plasma frequency \( \omega_p \) is defined as:

\[ \omega_p = \left( \frac{n_e e^2}{\varepsilon_0 m_e^*} \right)^{1/2} \]  

(4.13)

Eq. (4.12) is frequently referred to as the Lorentz model dielectric constant. The real and imaginary parts of \( \varepsilon \) are written

\[ \varepsilon_1(\omega) = 1 + \frac{\omega_p^2 (\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \omega^2\Gamma^2} \]  

(4.14)

\[ \varepsilon_2(\omega) = \frac{\omega_p^2 \omega\Gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2\Gamma^2} \]

The optical properties of ionic crystals and inter-band transitions of valence electrons can be described very well with the Lotentz model.
4.1.3 The Drude Model: Oscillator Model for Free Electrons

The Drude model assumes a free electron gas oscillating in the electromagnetic field. The designation "free" means that the restoring force representing the "bound" effect in the Lorentz model is absent, i.e. $\omega_0 \approx 0$. By introducing a scattering time $\tau_{sc} = 1/\Gamma$, Eq. (4.12) in this case becomes

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega/\tau_{sc}}$$

(4.15)

and separating the real and imaginary part gives

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2 \tau_{sc}^2}{1 + \omega^2 \tau_{sc}^2}$$

(4.16)

$$\varepsilon_2(\omega) = \frac{\omega_p^2 \tau_{sc}}{\omega (1 + \omega^2 \tau_{sc}^2)}$$

Eq. (4.15) and Eq. (4.16) are usually referred to as the Drude model optical constants. In the relatively high frequency range $\omega \sim \omega_p$, if damping is negligible i.e. $\hbar/\tau_{sc} \ll \hbar \omega, \hbar \omega_p$, then $\varepsilon(\omega)$ is progressively real, and expressed as:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

(4.17)

The Drude model is extensively used to describe optical properties of materials with free electron-like properties, such as alkali metals, noble metals, IIIA metals, some transition metal nitrides, TCOs etc.

4.1.4 The Oscillator Model for Real Materials

The dielectric constant of real insulating materials usually contains several Lorentz oscillators; that of metallic materials contains one additional Drude term. All of these effects are additive so we have for insulators

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_n \frac{A_n}{\omega_n^2 - \omega^2 - i\omega/\tau_{sc,n}}$$

(4.18)

and for metals:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_n \frac{A_n}{\omega_n^2 - \omega^2 - i\omega/\tau_{sc,n}} - \frac{\omega_p^2}{\omega^2 + i\omega/\tau_{sc}}$$

(4.19)
where $\omega_n$ and $A_n$ correspond to characteristic band-to-band transition energies and their spectral weight, respectively. $1/\tau_{sc,n}$ is proportional to the width of each transition and $\varepsilon_\infty$ represents the dielectric background as a result of the contribution from core electrons (bound charges). Typically, $1 \leq \varepsilon_\infty \leq 10$.

### Screened plasma frequency: the famous example of silver

Calculations based on the electron density of Ag from Eq. (4.13) leads to $\omega_p = 9.2$ eV as the energy where $\varepsilon_1$ is expected to approach 0. However, the positive contribution from bound charges from below 6 eV lifts up the $\varepsilon_1(\omega)$ v.s. $\omega$ curve so that the $\varepsilon_1(\omega)$ crosses 0 at 3.9 eV instead of at 9 eV. This new plasma frequency $\omega_p^*$ is called the screened plasma frequency and can be obtained by

$$\omega_p^* = \frac{\omega_p}{\sqrt{\varepsilon_\infty}}$$

(4.20)

At this frequency the free electron approximation of $\varepsilon(\omega)$, at relatively high frequency provided with negligible damping $\hbar/\tau_{sc} \ll \hbar \omega, \hbar \omega_p$, expressed as:

$$\varepsilon(\omega) = \varepsilon_\infty \left(1 - \frac{\omega_p^{*2}}{\omega^2}\right)$$

(4.21)

go to 0.

Silver has $\varepsilon_\infty \sim 5$, $\hbar \omega_p \sim 9.2$ eV, $\hbar/\tau_{sc} \sim 0.02$ eV. $\hbar \omega_p^*$ is then obtained to be $\sim 4.1$ eV, not that far from the observed 3.9 eV.

### 4.1.5 Size-dependent Dielectric Functions

Here we consider particle sizes in the nano realm, i.e., much smaller than wavelength. The same quantum confinement effect as observed in semiconductor nanocrystals quantum dots is usually negligible in metal nanoparticles [95]; instead, the confinement effect on the electron mean free path value $\ell$ plays a significant role in the optical response. The mean free path $\ell$ is defined as the path length that the electron travels between two successive scattering events, defined as:

$$\ell = v_F \tau_f$$

(4.22)
with $v_{Ff}$ being the Fermi velocity and $\tau_f$ being the mean scattering time in thin films (or bulk).

The extra scattering events against the particle boundary give increasing contributions to the plasma damping (reduces the mean scattering time $\tau_f$) as the size of the particles gets smaller, and may even become dominating when the size gets smaller than $\ell$. This confinement effect of particle boundary can be quite profound in metals like Cu, Ag, Au with room temperature values $\ell \sim 42, 52$ and $42$ nm, respectively. The mean scattering time $\tau_p$ in metallic nanoparticles can be written as a function of the particle diameter $D_p$:

$$\frac{1}{\tau_p} = \frac{1}{\tau_f} + \frac{2v_F}{D_p}$$  (4.23)

If the dielectric function for thin films or the bulk $\varepsilon_f$ is given, the dielectric function corrected for particle size $\varepsilon_p$ can be written as:

$$\varepsilon_p = \varepsilon_f - \varepsilon_f^D + \varepsilon_p^D$$  (4.24)

where the Drude (D) type terms are given by:

$$\varepsilon_f^D = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau_f)}$$  (4.25)

and

$$\varepsilon_p^D = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau_p)}$$  (4.26)

Here $\omega_{p,f}$ denotes the plasma frequency in particles or films. The above procedure can be found in literature [96].

It is known that the dielectric function of particles is not necessarily the same as that of bulk, therefore a discussion based on Eq. (4.23) is necessary in order to determine an appropriate $\varepsilon_p$ for particles. For such discussions, it is convenient to rewrite Eq. (4.23) as

$$\tau_p = \frac{\tau_f}{1 + \frac{2v_F}{D_p} \tau_f} = \frac{\tau_f}{1 + \frac{2\ell_f}{D_p}}$$  (4.27)

with $\ell_f$ being the electron mean free path in the film. It is given by $\ell_f = v_{Ff} \tau_f$.

For noble metals in which electrons have a high Fermi velocity and large mean free path, the term $\frac{2v_F}{D_p} \tau_f$ (i.e., $\frac{2\ell_f}{D_p}$) can be large and the procedure of
Eq. (4.24) is necessary. In contrast, for materials with electron mean free paths \( \ell_f \ll D_p \), the term \( \frac{2v_F f \tau_f}{D_p} \) is negligible, so that we have \( \tau_p = \tau_f \) and thus \( \varepsilon_p = \varepsilon_f \).

### 4.2 Effective Medium Models for Nanoparticles and Composite Coatings

A composite coating is one class of inhomogeneous material. For the optical property of such a material, the quasistatic approximation is valid if the size of inhomogeneity (e.g. particles, clusters etc) satisfies the condition [97]:

\[
\pi \varepsilon_{\text{max}}^{1/2} \frac{D_p}{\lambda} \ll 1
\]  

(4.28)

where \( D_p \) is the diameter of the particle inclusions in the composite and \( \varepsilon_{\text{max}} \) denotes the largest of the dielectric functions in the material.

This means that the particle is so much smaller than the wavelength, so that the electromagnetic field in the particle is approximately constant. If the inhomogeneity also produces no scattering, the composite material containing such inhomogeneities can be considered to have the same optical properties as an homogenous material, i.e., the probing light of sufficiently large wavelength cannot tell the difference between the two. The optical property of the inhomogeneous material can be replaced by those of an homogenous material characterized by an effective dielectric function \( \varepsilon_{\text{eff}} \). Such an inhomogeneous material can be considered to be an "effective medium". The effective medium theory is developed to offer a view on the homogenized optical response of this kind of composite material, based on mean field theory.

The inhomogeneities in such materials can have different microstructures and the approximation scheme for the optical properties should be chosen accordingly. The general approach is as follows: for microstructures comprised of isolated particles, the Maxwell-Garnett theory [98, 99] is appropriate; for microstructures containing topologically equivalent units, the Bruggeman theory [100] should be used instead. The derivation of the Maxwell-Garnett theory and the Bruggeman theory for optical properties can be found in the literature [101]. Both theories can be generalized to approximate for other physical properties such as electronic conductivity, heat conductivity etc. Here we limit the discussion to their application for optical properties.

It is well-known that nanocomposite materials can have novel optical properties that are non-existing in film or bulk. The effective medium theory pertains to a small particle limit and offers an approximate guideline for spectral tuning of optical properties of nanoparticle composites. This is discussed at the end of this chapter.
4.2.1 The Maxwell-Garnett Theory

The Maxwell-Garnett theory [98, 99] is widely used for estimating optical properties of composite layers containing isolated particles. It works best when the particle filling factor \( f \) (i.e. volume fraction) is small, such as in the case of a dilute suspension of nanoparticles in a matrix [102, 103].

Here we describe the procedures for applying the Maxwell-Garnett theory used in this work. Given that the particle sizes are much smaller than the wavelength as described by Eq. (4.28), the particles are far enough from each other not to invoke particle-particle interactions. The Maxwell-Garnet theory can be used to obtain the effective dielectric function \( \varepsilon_{MG} \) by

\[
\varepsilon_{MG} = \varepsilon_m \frac{1 + \frac{2}{3} f \alpha_{pol}}{1 - \frac{2}{3} f \alpha_{pol}}
\]

where \( \varepsilon_m \) is the dielectric function of the matrix and \( f \) is the "filling factor" i.e., the volume fraction occupied by the particles. The parameter \( \alpha_{pol} \) is the polarizability of the particles, which depends on the shape and arrangement of the particles.

4.2.1.1 Solid Spheroids

For aligned solid spheroidal particles, as discussed in Chapter 7.1, the polarizability and can be written

\[
\alpha_{pol} = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_m + L (\varepsilon_p - \varepsilon_m)}
\]

where \( \varepsilon_p \) is the dielectric function of the particles and the parameter \( L \) is the appropriate depolarization factor, which takes particle shape into account. For randomly oriented ellipsoidal particles, as shown in Fig. 4.1 (d), \( \alpha_{pol} \) can be obtained by averaging \( \alpha_{pol} \) over the three principal axes of the ellipsoid according to

\[
\alpha_{pol} = \frac{1}{3} \sum_{i=1}^{3} \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_m + L_i (\varepsilon_p - \varepsilon_m)}
\]

where \( L_i \) denotes the depolarization factors along their three principal axes.

The depolarization factors \( L_i \) fulfill \( \sum L_i = 1 \). Spheres, as shown in Fig. 4.1 (a), have \( L_1 = L_2 = L_3 = 1/3 \). The aspect ratio \( m \) is defined in Fig. 4.1 as well. Spheres have \( m = 1 \). Oriented nanoparticles with spheroidal shapes with \( m \neq 1 \), as shown in Fig. 4.1 (b) and (c), can be taken into account by modifying the depolarization factor \( L \) as follows:
For prolate spheroids (PS) with $L_1 < L_2 = L_3$ and $m > 1$, the depolarization factors are related to the major (a) and minor axes (c) of the spheroids by [104]

$$L_1 = \frac{1 - e_{PS}^2}{2e_{PS}^2} \left( \ln \frac{1 + e_{PS}}{1 - e_{PS}} - 2e_{PS} \right)$$

(4.32)

and $L_2 = L_3 = (1 - L_1)/2$, where

$$e_{PS} = \left[1 - (c/a)^2\right]^{1/2}$$

(4.33)

For oblate spheroids (OS) with $L_1 = L_2 < L_3$ and $m < 1$, the depolarization factors are related to the major (a) and minor axes (c) of the spheroids by [104]

$$L_3 = (e_{OS}^3 + e_{OS}^{-1})(e_{OS} - \arctan e_{OS})$$

(4.34)

and $L_1 = L_2 = (1 - L_3)/2$ where

$$e_{OS} = \left[(a/c)^2 - 1\right]^{1/2}$$

(4.35)

For the situations shown in Fig. 4.1 (b) and (c), in which light is incident normal toward the layers with oriented nanoparticles with the electric field orthogonal to the high-symmetry axes of the nanoparticles, the depolarization factors are $L_3$ and $L_1$, respectively.

### 4.2.1.2 Nanoparticle Aggregates

In real nanoparticle samples, it is not certain that all the nanoparticles are perfectly dispersed and homogenously distributed. Particles can stick, to form chains and clusters, and thus dipole-dipole interaction between the particles can no longer be disregarded. Fortunately, the optical properties of such particle aggregates can be estimated. Previous studies [103] have shown that one can construct effective depolarization factors $L_{i,\text{eff}}$ from examining the resonance characteristics of the aggregates [105] to represent the dipole-dipole interaction effect. $L_{\text{eff},i}$ for several geometrical configurations extracted by the literature [103] are shown in Table 4.1

Unlike the spheroids, the effective depolarization factor $L_{\text{eff},i}$s of particle aggregates does not add up to unity, but rather satisfies the relation $\sum L_{\text{eff},i} \sim 1$. This approach was used in paper VIII to calculated the optical properties of chains and fcc clusters of ITO particles dispersed in polymer electrolyte.

### 4.2.1.3 Core-shell structures

For randomly-oriented core-shell nanoparticles the polarizability $\alpha_{\text{pol}}$ is given by
Figure 4.1: Schematic drawings for composites of solid nanoparticles with a dielectric function $\varepsilon_p$ embedded in a medium with dielectric function $\varepsilon_m$. The nanoparticles are taken to be spherical (a), oriented prolate (b), oriented oblate (c), and random prolate and oblate (d) with major axis $a$ and minor axis $c$ respectively. An aspect ratio $m$ is defined for prolate and oblate spheres.
Table 4.1: Equivalent depolarization factors $L_{\text{eff},i}$ for shown geometrical configurations of nanoparticles determined by literature.[103]

<table>
<thead>
<tr>
<th>Geometrical Configuration</th>
<th>$L_{\text{eff},1}$</th>
<th>$L_{\text{eff},2}$</th>
<th>$L_{\text{eff},3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single sphere</td>
<td>1/3</td>
<td>1/3</td>
<td>1/3</td>
</tr>
<tr>
<td>Double sphere</td>
<td>0.250</td>
<td>0.375</td>
<td>0.375</td>
</tr>
<tr>
<td>Single strand chain</td>
<td>0.133</td>
<td>0.435</td>
<td>0.435</td>
</tr>
<tr>
<td>Double strand chain</td>
<td>0.139</td>
<td>0.342</td>
<td>0.518</td>
</tr>
<tr>
<td>fcc lattice</td>
<td>0.0865</td>
<td>0.0865</td>
<td>0.827</td>
</tr>
</tbody>
</table>

\[ \alpha_{\text{pol}} = \frac{1}{3} \sum_{i=1}^{3} \frac{(\varepsilon_s - \varepsilon_m)(\varepsilon_s + (\varepsilon_c - \varepsilon_s)(L_{c_i}^c - \Omega L_{s_i}^s)) + \Omega \varepsilon_s (\varepsilon_c - \varepsilon_s)}{\varepsilon_s + (\varepsilon_c - \varepsilon_s)(L_{c_i}^c - \Omega L_{s_i}^s)} \left[ \varepsilon_m - L_{c_i}^c (\varepsilon_m - \varepsilon_s) \right] + \Omega L_{s_i}^s \varepsilon_s (\varepsilon_c - \varepsilon_s) \right] \]  

(4.36)

where $\varepsilon_c$, $\varepsilon_s$ and $\varepsilon_m$ are the dielectric functions of the core (i.e. inner spheroid) with depolarization factors $L_{c_i}^c$, the shell (i.e. coating around the spheroid) with depolarization factors $L_{s_i}^s$ and the surrounding medium. $\Omega$ is the volume ratio between the inner and outer spheroids. By putting $\Omega = 1$ and $L_{c_i}^c = L_{s_i}^s = L_i$ in Eq. (4.36), $\varepsilon_s$ would cancel out between the numerator and the denominator and we would have the expression for randomly-oriented solid spheroids Eq. (4.31) with $\varepsilon_c$ equivalent to $\varepsilon_p$ in Eq. (4.31).

In this thesis, we used spherical core shell particles with $L_{c_i}^c = L_{s_i}^s = 1/3$ as shown in Fig. 4.2. Eq. (4.36) can then be simplified to:

\[ \alpha_{\text{pol}} = \frac{3}{3} \frac{(\varepsilon_s - \varepsilon_m)(\varepsilon_c + 2\varepsilon_s) + \Omega (2\varepsilon_s + \varepsilon_m)(\varepsilon_c - \varepsilon_s)}{(\varepsilon_s + 2\varepsilon_m)(\varepsilon_c + 2\varepsilon_s) + \Omega (2\varepsilon_s - 2\varepsilon_m)(\varepsilon_c - \varepsilon_s)} \]  

(4.37)

with

\[ \Omega = \left( \frac{x}{x+2t} \right)^3 \]  

(4.38)

where $x$ is the diameter of the core and $t$ is the thickness of the shell.

Requiring the volume fraction of the material composing the shell to be 0.01, as discussed in Chapter 7.2, the filling fraction of the particles $f$ is

\[ f = 0.01/(1 - \Omega) \]  

(4.39)
Figure 4.2: Structural model representing core-shell nanoshells in a surrounding medium under irradiation of photons with energy $h\omega$.

4.2.2 The Bruggeman Theory

For structures with non-isolated particles and topologically equivalent components, the Bruggeman theory [100, 101] is the appropriate approach used for obtaining the effective dielectric function. The Bruggeman theory may hold well when the filling factor is varied from 0 to 1. It can also account for the optical effects when $f$ is varied across the percolation threshold [11]. Due to these merits, the Bruggeman theory is a very widely used effective medium theory for optical properties.

According to the Bruggeman theory, for a two-component composite layer with spherical structural units the effective dielectric function $\varepsilon^{BR}$ can be written

$$f \frac{\varepsilon_A - \varepsilon^{BR}}{\varepsilon_A + 2\varepsilon^{BR}} + (1 - f) \frac{\varepsilon_B - \varepsilon^{BR}}{\varepsilon_B + 2\varepsilon^{BR}} = 0 \quad (4.40)$$

where $\varepsilon_A$ and $\varepsilon_B$ are the dielectric functions of the two components A and B, and $f$ is the filling factor of A.

This equation is the one used to calculate for results in Chapter 7.3. The solution of Eq. (4.40) was obtained by using the approach developed by Berthier and Lafait [106]. An extension to n-component composites can be found in works by Jansson and Arwin [107].
The Bruggeman theory can be extended to randomly oriented spheroids with dielectric function $\varepsilon_p$ and triplet of depolarization factors $L_i$ s densely distributed in a medium composed of spherical particles with dielectric function $\varepsilon_m$. In this case, $\varepsilon^{BR}$ is given by:

$$\varepsilon^{BR} = \frac{\varepsilon_m}{1 - \frac{1}{3} f \alpha_{pol}^{BR}} + \frac{2}{3} f \alpha_{pol}^{BR} \tag{4.41}$$

and parameter $\alpha_{pol}^{BR}$ is expressed as:

$$\alpha_{pol}^{BR} = \sum_{i=1}^{3} \frac{\varepsilon_p - \varepsilon^{BR}}{\varepsilon^{BR} + L_i (\varepsilon_p - \varepsilon^{BR})} \tag{4.42}$$

where $L_i s$ can be obtained from Eq.s (4.32), (4.33) for prolate spheroids and Eq.s (4.34), (4.35) for oblate spheroids.

### 4.2.3 Tuning the Optical Property of Metallic Nanoparticles

The well-known fact that nanoparticle composites can have different properties from those of the bulk lies at the heart of recent technological advances in nanophotonics. The optical response of metallic nanoparticles is influenced by the dielectric function of the particles and the surrounding medium as well as by the size and shape. Here is a brief description of how it works.

Under irradiation of an alternating electro-magnetic field, the free electrons in a metallic nanoparticle oscillate following the external field and give rise to polarization oscillating along the field characterized by the dipole moment $p$. The dipole moment $p$ is a measure of the optical response of a single nanoparticle; when $p$ has a peak, the nanoparticle has a plasmon resonance. In the quasi-static picture inherent in the effective medium theories, described earlier in this chapter, the nanoparticles have a dipole moment $p$ that is proportional to the polarizability $\alpha_{pol}$. So for a single nanoparticle or dilutely distributed nanoparticles ($f \to 0$) the resonance condition is $\alpha_{pol}(\omega) = \alpha_{pol,\text{max}}$. In other words, when the denominator in the expression of $\alpha_{pol}$ becomes a minimum, a plasmon resonance will occur which results in a strong absorption of light.

For solid spheroids, one can see that in Eq. (4.30) and (4.31) $\alpha_{pol}$ is related to $\varepsilon_m$, $\varepsilon_p$ and $L_i$. Thus, by changing the materials used for the embedding matrix and the particles as well as the shape of the particles, the spectral tuning of plasmon absorption can be achieved. The resonance condition for spheres is $\varepsilon_p = -2\varepsilon_m$ at dilute limit ($f \to 0$). Aligned spheroids have one resonance frequency, whereas randomly oriented spheroids have two resonance frequencies.
The same occurs for core-shell particles in Eq. (4.36). By altering the materials for the core $\varepsilon_c$, shell $\varepsilon_s$ and the medium $\varepsilon_m$, the shape of the particles via $L_i$ as well as the volume ratio between the core and the outer sphere $\Omega$, one can spectrally tune the plasmon absorption. Moreover, the additional parameter $\Omega$ offers a much broader range of spectral tuning compared to solid spheres. An example of powerful spectral tuning offered by core-shell nanoparticles is shown in Figure 3.11 of Ref [11], in which silica-Ag-core-shell nanoparticles with different silver shell thickness enabled spectral tuning of plasmon absorption across the solar spectrum.

A more detailed treatise on plasmonics can be found in Ref. [95].

Surface plasmon resonance of metallic state VO$_2$ nanoparticles

The localized dipole surface plasmon resonance of a single metallic particle or metallic nanoparticles at dilute limit ($f \to 0$) happens when the polarizability defined by Eq. (4.30) reaches maximum, which requires approximately:

$$\varepsilon_p(\omega) = -2\varepsilon_m$$  \hspace{1cm} (4.43)

for spheres with $L_1 = L_2 = L_3 = 1/3$, provided $\varepsilon_p^2 \ll 1$. This is known as the Fröhlich condition. [52]. Some Drude parameters of VO$_2$ are available from literature [108] roughly $\varepsilon_\infty \sim 4.5$, $\hbar \omega_p \sim 3.5$ eV, and $\hbar/\tau \sim 0.7$ eV. Applying $\varepsilon_m = 2.25$, the assumption of the damped Drude model in Eq. (4.16) combined with Eq. (4.43) gives a rough estimation of the localized surface plasma resonance frequency $\hbar \omega_{\text{res}} = 0.93$ eV (around 1333 nm), where significant light absorption occurs. This phenomenon is the basis for the idea of Nanothermochromics.
This box gives a rough evaluation of plasma frequency and electron density of experimentally prepared ITO nanoparticles from optical absorbance measurements - an important but unpublished procedure in work featured in Paper VIII [109]. According to the Fröhlich condition Eq.(4.43), and Drude dielectric function expressed with screened plasma frequency Eq.(4.21), the resonance frequency of dilutely distributed ITO particles $\omega_{\text{res}}$ should roughly satisfy the condition

$$\varepsilon_\infty (1 - \frac{\omega_p^2}{\omega_{\text{res}}^2}) = -2\varepsilon_m$$  \hspace{1cm} (4.44)

thus

$$\omega_p^2 = \omega_{\text{res}}^2 \sqrt{1 + \frac{2\varepsilon_m}{\varepsilon_\infty}}$$  \hspace{1cm} (4.45)

One can make a very rough estimation of $\omega_p$ of ITO from the optical absorbance measurement performed on a system consisting of ITO nanoparticles dilutely embedded in a glass or polymer-like dielectric medium, as studied in Paper VIII [109]. The experimental optical absorbance data in Fig. 1 of the paper suggest that the localized plasmon absorption of the nanoparticle composite is located at $\lambda \sim 1850$ nm, equivalent to $\hbar \omega_{\text{res}} \sim 0.67$ eV. From literature [16], it can be found that ITO has $\varepsilon_\infty \sim 4$, $m^*_e \sim 0.35$, the embedding medium is taken to have $\varepsilon_m \sim 2.25$, then from Eq. (4.45), the screened plasma frequency of ITO is roughly estimated to be $\hbar \omega_p^* \sim 0.99$ eV, and from Eq. (4.20), the plasma frequency (non-screened) is $\hbar \omega_p \sim 1.98$ eV. From Eq. (4.13), the electron density can be estimated as $n_e \sim 9.2 \times 10^{20}$ cm$^{-3}$. After further fine tuning compared with experimental data, the electron density was determined to be $n_e \sim 9.8 \times 10^{20}$ cm$^{-3}$.

### 4.3 Thin Film Optics

#### 4.3.1 One Interface: Fresnel Equations

As illustrated in Fig. 4.3, consider an interface between medium 1 and 2 with corresponding refractive indices $N_1$ and $N_2$, respectively; the angles of incidence and transmittance are $\theta_1$ and $\theta_2$, respectively. The boundary condition
at the interfaces states that the normal component of the B-field and the tangential component of the E-field are continuous at the interface. By applying this boundary condition to Maxwell equations, we get Fresnel equations:

\[
\begin{align*}
    t_p &= \frac{2N_1 \cos \theta_1}{N_1 \cos \theta_2 + N_2 \cos \theta_1} \\
    t_s &= \frac{2N_1 \cos \theta_1}{N_1 \cos \theta_1 + N_2 \cos \theta_2} \\
    r_p &= \frac{N_2 \cos \theta_1 - N_1 \cos \theta_2}{N_1 \cos \theta_2 + N_2 \cos \theta_1} \\
    r_s &= \frac{N_1 \cos \theta_1 - N_2 \cos \theta_2}{N_1 \cos \theta_1 + N_2 \cos \theta_2}
\end{align*}
\] (4.46)

where \( t \) and \( r \) denote the interface amplitude transmittance and reflectance. Subscripts \( s \) and \( p \) denote the polarization of light. The angles \( \theta_1 \) and \( \theta_2 \) are related by Snell’s law:

\[
N_1 \sin \theta_1 = N_2 \sin \theta_2
\] (4.47)

The Fresnel equations in Eq. (4.46) can be written alternatively without \( N_1 \) and \( N_2 \) as
\[ t_p = \frac{2 \sin \theta_2 \cos \theta_1}{\sin(\theta_1 + \theta_2) \cos(\theta_1 - \theta_2)} \]

\[ t_s = \frac{2 \sin \theta_2 \cos \theta_1}{\sin(\theta_1 + \theta_2)} \]

\[ r_p = \frac{\tan(\theta_1 - \theta_2)}{\tan(\theta_1 + \theta_2)} \]

\[ r_s = -\frac{\sin(\theta_1 - \theta_2)}{\sin(\theta_1 + \theta_2)} \]

The intensity transmittance and reflectance are given by

\[ T_{s,p} = \frac{N_2 \cos \theta_2}{N_1 \cos \theta_1} t_{s,p} t_{s,p}^* \]

\[ R_{s,p} = r_{s,p} r_{s,p}^* \] (4.49)

### 4.3.2 Two Interfaces

In this section, both s and p-polarization give the same expressions so the subscripts "s" and "p" are omitted. Light interacting with a **coherent layer** exhibits interference. The total amplitude transmittance and reflectance should be obtained by summing up amplitude contributions from multiply reflected light taking into account the phase. Consider a single coherent layer with thickness \(d\), composed of medium 2 characterized by refractive index \(N_2\) between two media 1 and 3 characterized by refractive index \(N_1\) and \(N_3\) as shown in Fig. 4.4. Amplitude reflectance is denoted by \(r_1\) for interface 1/2, \(r'_1\) for interface 2/1, \(r_2\) for interface 2/3; amplitude transmittance is denoted by \(t_1\) for interface 1/2, \(t'_1\) for interface 2/1, \(t_2\) for interface 2/3. In addition a phase change \(\delta = -\frac{2\pi}{\lambda} N_2 d \cos \theta_2\) occurs during the passage of light in the film.

Summing up the contribution from each transmittance and reflectance and taking into the account the phase change \(\delta\), we have for total amplitude reflectance

\[ r_{coh} = r_1 + t_1 t'_1 r_2 \exp(-2i\delta) + t_1 t'_1 r'_1 r_2^2 \exp(-4i\delta) + ... \]

\[ = r_1 + \frac{t_1 t'_1 r_2 \exp(-2i\delta)}{1 - r'_1 r_2 \exp(-2i\delta)} \] (4.50)
with \( r'_1 = -r_1 \) and \( t_1t'_1 = 1 - r_1^2 \), the final form of Eq. (4.50) is written:
\[
 r_{coh} = \frac{r_1 + r_2 \exp(-2i\delta)}{1 + r_1r_2 \exp(-2i\delta)}
\]

(4.51)

Similarly, the total amplitude transmittance is
\[
 t_{coh} = t_1t_2 \exp(-i\delta) + t_1t_2r'_2r_2 \exp(-3i\delta) + t_1t_2r'_1r_2^2 \exp(-5i\delta) \ldots
\]
\[
 = \frac{t_1t_2 \exp(-i\delta)}{1 + r_1r_2 \exp(-2i\delta)}
\]

(4.52)

The intensity transmittance and reflectance in this coherent two-interface case are
\[
 T = \frac{N_3 \cos \theta_3}{N_1 \cos \theta_1} t_{coh}^* t_{coh}^*
\]
\[
 R = r_{coh} r_{coh}^*
\]

(4.53)

In the incoherent layer, the phase coherence is lost when light is passing through the material. The total intensity transmittance and reflectance are obtained by adding up intensity contributions of multiply reflected light without considering their phase. With the same configurations as in Fig. 4.4, consider an incoherent layer with thickness \( d \), composed of a material denoted
2 characterized by \(N_2\) placed in between medium 1 and 3. The bulk intensity reflectance is denoted \(R_1\) for interface 1/2, \(R'_1\) for interface 2/1, \(R_2\) for interface 2/3; the bulk intensity transmittance is denoted \(T_1\) for interface 1/2, \(T'_1\) for interface 2/1, \(T_2\) for interface 2/3. We have \(T_1 = T'_1\). Replacing amplitude transmittance and reflectance with bulk intensity transmittance and reflectance, phase term \(-i\delta\) with absorption \(-\alpha d\) in Eq. (4.50) and Eq. (4.52), we can obtain the total intensity reflectance and transmittance \(R\) and \(T\):

\[
R = R_1 + \frac{T_1^2R_2\exp(-2\alpha d)}{1 - R'_1R_2\exp(-2\alpha d)}
\]

\[
T = \frac{T_1T_2\exp(-\alpha d)}{1 - R'_1R_2\exp(-2\alpha d)}
\]  

(4.54)

### 4.3.3 More Interfaces: Multilayer Films

For multilayer films, the calculation requires matrix multiplications based on the transfer matrix method that can be found in standard textbooks on optics [110–112]. The procedure that we use in this study is a transfer matrix method based on work by Pfrommer et al. [113]. Two kinds of matrices corresponding to possible transformation of the radiation field are considered:

**Interface matrix** denoted by \(M\), corresponding to transmission of the radiation field or intensity across an interface. Here the boundary conditions at the interface are considered.

**Layer matrix** denoted by \(S\), corresponding to the transmission of the radiation field through a layer. Here the phase change and the attenuation of the radiation field or the intensity is considered, depending on the layer thickness.

The total transmittance \(T_{oi}\) and reflectance \(R_{oi}\) from outer halfspace \(i\) to inner halfspace \(o\) can be solved from relation:

\[
\begin{bmatrix}
1 \\
R_{oi}
\end{bmatrix} = M_{o,1}S_1M_{1,2}S_2...S_{q-1}M_{q-1,1}qS_qM_{q,i} \begin{bmatrix}
T_{oi} \\
0
\end{bmatrix}
\]

(4.55)

The detailed procedure is described in literature [113, 114]
5. Experimental Methods

An expert is a person who has found out by his own painful experience all the mistakes that one can make in a very narrow field.

Niels Bohr

5.1 Sample Fabrication: DC Magnetron Sputtering

In the DC sputtering process, the targets are connected to the cathode and the substrate and the chamber walls are grounded. Argon (Ar) gas is introduced and ionized by the electric field into plasma containing energetic Ar ions that bombard the target surface, which leads to the deposition of target atoms on the substrate. Besides Ar, reactive gas species (such as oxygen and nitrogen etc.) can be introduced to promote chemical reactions to form compounds as the end product of the deposition; this process is called DC reactive sputtering.

In the magnetron sputtering process, magnets are strategically installed behind the target to generate magnetic fields that can effectively confine beam electrons into helix motions following an orbit trail near the target surface, and enhance the path length of the electrons so that the they can ionize more Ar before escaping. Thus, the application of magnetron sputtering can help sustain the plasma with much lower pressure, and greatly improve the deposition rate.

The reactive DC magnetron sputtering process used in works presented in this thesis took place in a vacuum system based on Balzers UTT 400 unit, as shown in Fig. 5.1, and the inside geometry of the chamber is shown in Fig. 5.2. For thin film fabrications, the setup of a downward-directing tube oxygen inlet as shown in Fig. 5.2 (a) was used. Other setup of oxygen inlets are available, as shown in Fig. 5.2 (b) and (c), for the fabrication of samples with more porous morphologies, as is be discussed in Section 5.1.2. The substrates (1-mm-thick slide glass from the maker "Thermo Scientific") were put on a rotating holder located 13 cm from the 5-cm-diameter V (99.5%) at an oblique angle, with 50° between the substrate surface normal and the average direction of the sputtered target atom flux. For doping purposes, Mg target (99.9%) can be installed at a slot equivalent to the V target, as shown in Fig. 5.2 (a).
5.1.1 The Sputtering of Pure and Mg-doped VO$_2$ Films

The deposition chamber was pumped down to $6.3 \times 10^{-7}$ mbar before heating the substrates. The substrates were subsequently heated to $\sim 450 \pm 10$ °C as estimated from thermocouple readings. 80 ml/min of Ar and $\sim 5$ ml/min of O$_2$ (both 99.997%) were then introduced via mass-flow-controlled inlets, as in Fig. 5.2 (a). A total pressure of $\sim 9.2$ mTorr was maintained during film fabrication. Sputtering takes place at a power of 172 W and 0-57 W applied on the V target and Mg target, respectively. Films were grown at 0.05-0.06 nm/s to a thicknesses of 40-100 nm and on to glass and carbon substrates. Some films contained $\sim 0.45$ at.% Si from system contamination, which was later fixed with a new design of substrate holder.

5.1.2 The Sputter Deposition of VO$_2$ Nanorods

Sputter deposition of VO$_2$ nanorods was done to explores the influence of the temperature, thickness, substrate and geometry of reactive gas inlet on the growth morphology of VO$_2$. Sputter deposition takes place from the V target only and follows the same procedure as stated in 5.1.1, with a variety of setups of gas inlets, substrates and substrate temperatures. The O$_2$ gas inlets were of 3 different arrangements, as shown in Fig. 5.2: (a) a simple downward-directing tube (b) a perforated toroid gas inlet with holes obliquely facing the substrate (c) the same perforated toroid gas inlet flipped upside down compared to (b) with holes obliquely directing the gas away from the substrate. The substrates used in this study were of 3 kinds: (i) a 1-mm-thick glass slide from the maker "Thermo Scientific", which is the same as is used in VO$_2$ film production as described in Sect. 5.1.1; (ii) such glass coated with a 4.2-nm-thick gold film made by room temperature sputter depositon; (iii) glass coated with $\sim 50$-nm-diameter silica nanopillars made by glancing angle depositions topped with gold caps produced in Kyoto, as reported in literature [115]. The substrate temperature during the deposition was set at $450 \pm 10$ or $550 \pm 10$ °C.

Figure 5.1: The Magnetron sputter deposition chamber based on Balzers UTT 400 unit.
Figure 5.2: Target-substrate geometry inside the sputter chamber and the different setups for the O$_2$ gas inlet. (a) a simple downward-directing tube (b) a perforated toroid gas inlet directing gas toward the substrate (c) the toroid gas inlet directing the gas away from the substrate.
5.2 Rutherford Backscattering Spectrometry

Rutherford backscattering spectrometry (RBS) is a well-established ion beam technique for analyzing elemental composition, and it is especially powerful for detecting heavier atoms. The collision events between incident ions, usually proton or $^4$He$^+$ with MeV energy, and the target sample involves two main processes: the elastic scattering of incident ion by the target nuclei and the inelastic scattering of the incident ion by the electrons in the target. The former yields backscattered ions with energies depending on the mass of the target atoms, which is manifested as an abrupt onset of an edge or peak in the spectrum. The latter process gives rise to the energy loss of the impinging ion, which is proportional to the "stopping power" and the number of atoms per unit area of the target, and is manifested as the detailed shape of the spectrum adjacent to the low energy side of the edge or peak. In addition, the intensity of the backscattered ions is proportional to the number of target atoms in the detected area and their scattering cross section (the scattering cross section is proportional to the squared nuclear charge of the target atom). Thus, the information extracted from RBS reveals the stoichiometry and the number of atoms per unit area of the sample, and further more, the asymmetry of the peaks in the spectrum gives information about the "roughness" or "inhomogeneity" which is detected as a fluctuation in the number of atoms per unit area in the detected area. In high-resolution RBS, the use of low-energy ions can also give detailed depth profile down to atomic monolayers [116]. For more information on RBS mechanisms and techniques one should consult standard textbooks [117–120].

The samples studied in this work were measured in the Uppsala University tandem laboratory using 2 MeV $^4$He$^+$ ions as incidence and detected at a backscattered angle of 170°. Information such as stoichiometry, number of atoms per unit area and "roughness" were extracted by fitting the experimental spectra with simulated spectra using the SIMNRA program [121]. Examples of RBS results are shown in Fig. 5.3. The asymmetrical shape of the V peak in Fig. 5.3 (a) is due to fluctuation of V atom area density within the measured area as expected from nanorod samples. Fig. 5.3 (b) is an example fit for determining the value of Mg/(Mg+V) in the Mg-doped thin film samples.

If the elemental number fraction $n_i$ of atom $A_i$ with mass $m_i$, total atoms per area $N_{area}$ is known and the sample’s geometrical thickness $d$ is provided with another method, the mass density of the sample can be calculated:

$$\rho = \sum m_i n_i \times N_{area} / d \quad (5.1)$$

in which $n_i$ satisfies

$$\sum n_i = 1 \quad (5.2)$$
Figure 5.3: Experimental and simulated RBS data for a VO$_2$ nanorod sample on glass (sample No. 7 in paper IV)(a) and Mg-doped VO$_2$ thin film with shown Mg content (b).
5.3 X-ray Diffraction

X-ray diffraction [122–124] was used for studying the crystallographic structure of the samples. X-rays used in this technique typically have a wavelength of about 0.1 nm, comparable to the distance between crystal lattice planes. The diffraction arises from the interference effects which take place among the X-rays elastically scattered by the atoms in the crystal. The condition that allows the observation of the diffracted beam is roughly divided in two: i) the condition of constructive interference of scattered X-ray described by Bragg’s law:

\[ n_x \lambda = 2d_{hkl} \sin \theta_{scatter} \]  

(5.3)

where \( n_x \) is an integer that represents the order of diffraction, and \( d_{hkl} \) is the inter-planar distance of the planes with the Miller index \((hkl)\). \( 2\theta_{scatter} \) is the angle between the incident and diffracted beam.

ii) The condition that secures an observable intensity is governed by the scattering power of the atom species and their arrangement throughout the crystal lattice, which are collectively included in the expression of the structure factor \( F_{hkl} \), and related to the intensity of the peak as:

\[ I_{hkl} \propto |F_{hkl}|^2 \]  

(5.4)

Therefore, combining the above conditions i and ii, the Bragg reflection for a given wavelength of X-ray can be observed at \( 2\theta_{scatter} \) off the direction of the incident beam, provided that the intensity is not too weak to observe. By scanning the \( 2\theta_{scatter} \), one can obtain a diagram of peak intensity as a function of \( 2\theta_{scatter} \) that allows comparison with such crystallographic databases as the Inorganic Crystal Structure Database (ICSD) [125] or the Crystallography Open Database (COD) [126], etc., for the determination of the crystal structure of the sample.

The grazing incidence X-ray diffraction (GIXRD) data were recorded on the thin film and nanorod samples in the angle range of \( 10 < 2\theta_{scatter} < 80^\circ \) using a Siemens D5000 Th-2Th instrument and Cu Kα as the incidence beam. Rietveld refinement [127] using software PowderCell 2.3 program [128] was performed on the nanorod samples for the determination of preferred orientation using the March-Dollase model [129]. An example of XRD spectra and peak assignment is illustrated in Fig.5.4.
Figure 5.4: Glancing angle incidence X-ray diffraction taken at room temperature for VO$_2$ thin film and nanorod samples discussed in Paper IV. Samples 1 and 2 refer to the thin film samples with smaller and larger grains, respectively; samples 7 and 9 refer to nanorod samples with smaller and larger mass thickness, respectively.
5.4 Scanning Electrom Microscopy

Scanning electron microscopy (SEM) is a common method for observing sample morphology. When electrons impinge on the sample, the signal of backscattered electrons and the secondary electrons can be recorded. Repeating this process while scanning a sample area, the topological information in this area can be revealed by an intensity map of the recorded signal. The secondary electron signal is more informative about the topological contrast, whereas the backscatter electron signal emphasizes the compositional contrast, so one can choose which signal to detect accordingly. Such is the principle of the most basic SEM measurements.

In the study on nanorods, SEM was done using a LEO 1550 FEG Gemini instrument with an acceleration voltage of 5-15 kV and the secondary electron signals were collected. Surface images, cross section images, and a "bird-eye-view" image recorded with the sample surface normal tilted $70^\circ$ off the beam direction were recorded and discussed in 9.1. Examples of SEM images are shown in Fig. 5.5 for Mg-doped VO$_2$ films. These films have developed surface nanostructures.

![SEM images of Mg-doped VO$_2$ films](image)

*Figure 5.5: SEM image of Mg-doped VO$_2$ films with shown Mg/(Mg+V) atom ratio. (a) and (c) are the top views; (b) and (d) are the "bird-eye-view" imaged at 70° off the surface normal of the samples.*
5.5 Electrical Characterization: Sheet Resistance

Resistance measurement is done using the 4-wire method. The schematic setup is illustrated in Fig. 5.7. Samples were cut into bar shapes with four contacts painted on the thin film surface with silver glue. The contacts near the edges were connected to the power current supply with current readings $I$, and the inner contacts to the voltammeter with voltage readings $V$. The sampled area is the area between the two voltage contacts with resistance given by $R_{res} = V/I$, from which the resistivity $\rho_R$ can be obtained as:

$$\rho_R = \frac{R_{res}dL_{width}}{L_{length}} \quad (5.5)$$

where $L_{length}$ is the length dimension of the sampled area along the flow of current in the 4-wire method; $L_{width}$ is the width of the sampled area and $d$ is the thickness of the thin film sample.

In reality, the power, current and the voltmeter are contained by a KEITHLEY 2400 source meter in 4-wire sensing mode, so that the resistance of the measured area can be directly read and the resistivity can then be calculated using Eq. (5.5). The sample part was fixed on a heater controlled by a temperature controller connected to a thermometer. To correctly measure the sample temperature, the thermometer was fixed on top of a piece of glass substrate identical to that of the sample, located at an equivalent position as the 4-wire setup. The measured temperature range was 25-127 °C, with heating ramp rate 3 °C/min and cooling by turning off the heater.

The resultant resistivity curve as a function of temperature is shown in Fig. 5.6 for VO$_2$ thin films with different Mg-doping. The results shown in this figure are not consistent with trends of lowered $\tau_{cr}$ proportional to the Mg contents as established in literature [36, 42]. The reasons could be i) the number of samples measured was too small to establish a trend or i) the films have developed nanostructures (Fig. 5.5) that influenced the metal-to-insulator transition.
Figure 5.6: Resistivity as a function of temperature for shown VO$_2$ samples with shown Mg/(Mg+V) atom ratios.

Figure 5.7: Schematic drawing the the 4-wire measurement setup.
5.6 Optical Measurements

The measurement of UV/VIS transmittance and reflectance can be done using the absolute instrument and a Perkin Elmer Lambda 900 instrument. Both instruments use a white light source which passes through a monochromator.

![Figure 5.8: Schematic illustration of the absolute instrument.](image)

The absolute instrument [130] was used for measuring the specular component of transmittance and reflectance. The illustration is shown in Fig. 5.8. The advantage is that the reference data is taken on the primary beam itself and therefore free of the need for a reference plate. The drawback is that the intensity of the light source changes with time and frequent referencing is necessary. In this instrument, one first takes a reference by putting the detector at the "transmittance position" and keep sample out of the light path. Then transmittance and reflectance can be measured by putting the sample in the shown position in Fig. 5.8 and fixing the detectors at the "transmittance position" and "reflectance position" respectively. Angle-resolved reflectance measurements can be done with this instrument as well.

![Figure 5.9: Schematic illustration of the integration sphere.](image)

The Perkin Elmer Lambda 900 instrument is equipped with an integration sphere, as shown in Fig. 5.9, and it is capable of measuring total, specular, diffuse transmittance and reflectance. Ports 1, 2, 3, 4, 5 stand for transmittance port, reflectance port, exit port for specular reflectance, reference entry port and reference exit port, respectively. Referencing is done by recording the signal with incident light directly projected on the BaSO$_4$ reference sample.
fixed on port 2. All the measurements done in this study have port 4 open and port 5 closed so changes the instrument only involve ports 1, 2, 3.

1) Transmittance setting:

Measurement of signal $S_{1, tot}$: BaSO$_4$ reference sample is placed on port 2, and the sample is placed on port 1. Port 3 is closed.

Measurement of diffuse signal $S_{1, diff}$: a black cone is placed on port 2, and the sample is placed on port 1. Port 3 is closed.

Then the specular transmittance $T_{spec}$, diffuse transmittance $T_{diff}$ and total transmittance $T_{tot}$ can be obtained via:

$$T_{spec} = S_{1, tot} - S_{1, diff}$$

$$T_{diff} = S_{1, diff} \times R_{BaSO_4}$$

$$T_{tot} = T_{spec} + T_{diff}$$

Where $R_{BaSO_4}$ is the reflectance of the BaSO$_4$ reference recorded by the absolute instrument.

2) Reflectance setting:

Measurement of signal $S_{2, tot}$: sample is placed on port 2 with port 1 open and port 3 closed.

Measurement of diffuse signal $S_{2, diff}$: sample is placed on port 2 with port 1 open and port 3 open.

Here the specular transmittance $R_{spec}$, diffuse reflectance $R_{diff}$ and total reflectance $T_{tot}$ can be obtained via:

$$R_{spec} = (S_{2, tot} - S_{2, diff}) \times 0.96$$

$$R_{diff} = S_{2, diff} \times R_{BaSO_4}$$

$$R_{tot} = R_{spec} + R_{diff}$$

Where 0.96 is a factor to correct for the geometry of the integration sphere.

Optical properties of the thin film samples in this study were measured with the absolute instrument and Perkin Elmer Lambda 900 instruments. Some of the samples were rough and exhibited a small but non-negligible value of $R_{diff} \sim 5 \pm 2\%$ in the short wavelength end of the spectra. To suppress the influence of the surface roughness, reflectance was measured both from the substrate side and sample side to be used later in a fitting process for the determination of optical constants.

All the the nanorod samples were measured with the Perkin Elmer Lambda 900 instrument.
5.7 The Determination of Optical Constants

5.7.1 The Glass Substrate

In this study, the refractive index of the glass substrate was determined from *near-normal incidence* reflectance and transmittance of the 1-mm-thick glass substrate ("Thermo Scientific", identical to those used in experiments) recorded using the absolute instrument. Recall Eq.(4.54) in 4.3.2, when entrance and exit media have the same refractive index (both are air), \( N_1 = N_3 = 1 \), we have \( R_1 = R'_1 = R_2 \equiv \bar{R} \), \( T_1 = T_2 \equiv 1 - \bar{R} \) with \( \bar{R} = |(1 - n - ik)/(1 + n + ik)|^2 \), and Eq.(4.54) can be rewritten: [131]

\[
R = \bar{R} + \frac{(1 - \bar{R})^2 \bar{R} \exp(-2\alpha d)}{1 - \bar{R}^2 \exp(-2\alpha d)}
\]

(5.8)

\[
T = \frac{(1 - \bar{R})^2 \exp(-\alpha d)}{1 - \bar{R}^2 \exp(-2\alpha d)}
\]

Optical constants \( n \) and \( k \) can then be obtained in the following steps: [132]

\[
\bar{R} = \frac{(T^2 + 2) - (R - 1)^2}{2(2 - R)} - \sqrt{\left[\frac{(T^2 + 2) - (R - 1)^2}{2(2 - R)}\right]^2 - \frac{R}{2 - R}}
\]

\[
k = -\frac{\lambda}{4\pi d} \ln \left( \frac{R - \bar{R}}{RT} \right)
\]

(5.9)

\[
n = \left( \frac{1 + \bar{R}}{1 - \bar{R}} \right) \left( 1 + \sqrt{1 - \left( \frac{1 - \bar{R}}{1 + \bar{R}} \right)^2 (1 + k^2)} \right)
\]

The determined refractive index of glass is shown in Figure 5.10. This method was also documented in William E. Vargas’ PhD thesis [133].

5.7.2 Thin Films

The determination of optical constants of the thin film samples was done by simultaneously fitting the simulated transmittance and reflectance to the experimental ones. The procedure was achieved by using SCOUT software [134] based on a downhill simplex algorithm. SCOUT allows the building of multi-layer stack thin film models, typically, vacuum/thin film/substrate/vacuum for transmittance and reflectance collected from the sample surface side. For the
Figure 5.10: The optical constants $n$ (a) and $k$ (b) of the 1-mm-thick glass substrate determined using methods described in 5.7.1.

Figure 5.11: Experimentally measured and simulated spectral transmittance $T$ and reflectance recorded from the surface-coated side $R_s$ and substrate side $R_b$ of the VO$_2$ thin films with different Mg content as indicated in the figures. The upper panel is for the semiconducting state ($\tau < \tau_{cr}$) and the lower panel is for the metallic state ($\tau > \tau_{cr}$).
incoherent substrate layer, dielectric functions of the glass substrate shown in Fig. 5.10 were used. For the coherent thin film layer, models containing Brendel oscillators [134] (usually two in the 1-2 eV range, one in 3-4 eV range and one in further UV) were constructed for semiducting state; and models containing Brendel oscillators (usually one in 3-4 eV range, one in the near-infrared) combined with one drude term (for samples with high conductivity) were constructed for metallic state. The fitting parameters for the models are resonance frequencies, oscillator strength, damping and distribution width. The film thickness can also be determined by fitting.

As the films have surface roughness and small amounts of scattering in the short wavelength range, spectral transmittance $T$ and reflectance recorded from the sample side $R_s$ and the substrate side $R_b$ were used in the fitting. Two multilayer stacks were constructed with stack 1 configured as vacuum/thin film/substrate/vacuum, and stack 2 as vacuum/substrate/thin film/vacuum. The aim was to find one set of optical constants and thickness for the film to make a good fit of simulated spectra of stack 1 to $R_s$ and $T$ as well as stack 2 to $R_b$ and $T$ simultaneously. Another condition to ensure was that the film thickness determined on the semiconducting state must be identical to that of the metallic state. To fulfil this, the thickness was determined for both states separately first, and then the average of the two was fed back to the fitting procedure as a fixed value, followed by a refinement of the oscillator parameters. In this way, the thickness that fulfils agreement between measurements from the sample front side and substrate side, as well as between the semiconducting state and the metallic state, was determined with corresponding dielectric functions. An example of the fitting results yielded with this method is shown in Fig. 5.11 and the resultant $n$ and $k$ are shown in Fig. 5.12. This method is referred to as the "surface+back" method in the results part and in paper V. Some samples have developed nanostructures and could not yield a good fit with this method.
In the past, an old sets of $n$ and $k$ were determined by configuring one layer stack only: using the combination of $R_s$ and $T$ with layer stack vacuum/thin film/substrate/vacuum later referred to as the "surface" method, or with $R_b$ and $T$ using the layer stack vacuum/thin film/substrate/vacuum later referred to as the "back" method. In the case of "surface" or the "back" method, due to the fact that the only one layer stack was fitted, the constraint of matching the thickness of two layer stack configurations is relieved and therefore allowed those samples which did not yield a good fit with "surface+back" method to yield a good fit. As a result, the "back" method delivered good fits for 29 samples, whereas the "surface+back" methods only delivered good fits for 24 samples.

5.8 Determination of Band Gaps

The optical absorption coefficient is related to the imaginary part of the complex refractive index $k$, as $\alpha = 4\pi k/\lambda$, and the optical band gaps $E_g$ can be determined from:

$$ (\alpha h\nu)^m = A(h\nu - E_g) $$

where $h$ is Planck’s constant, $h\nu$ is the photon energy and A is a constant. The exponent $m$ depends on the nature of the optical transition and is taken to be $1/2, 1/3, 2, 2/3$ for indirect-allowed, indirect-forbidden, direct-allowed, and direct-forbidden optical transitions [135]. A plot of $(\alpha h\nu)^m$ as a function of $h\nu$ reveals band gap value as the intercept between axis $\alpha h\nu = 0$ and the linear fit near the onset of the absorption. In all the analyses in papers V and XIV, the indirect-allowed transition was assumed and therefore $m = 1/2$ was taken in the analysis. Two band gaps can be extracted, $\sim 0.5$ eV for the transition from lower $d_{||}$ to $\pi^*$ band and $\sim 1.6$ eV for that from O 2$p$ to $\pi^*$ band [22, 44]. The larger one $E_g \sim 1.6$ eV is relevant to the luminous properties of the films and was extracted from a large number of samples and discussed at length in paper V and 8.1. Fig. 5.13 shows example of band gap extraction described above for 2 Mg-doped samples with the assumption of different nature of transitions. The assumption of indirect allowed transition yielded 1.71 eV and 2.04 eV for Mg/(Mg+V)=0 and 0.088, respectively, whereas the corresponding figures for assuming direct allowed transition were 2.72 eV and 3 eV for Mg/(Mg+V)=0 and 0.088, respectively. It can be seen that the assumption of direct allowed transition yields $\sim 1$ eV larger value of $E_g$ than the assumption of indirect allowed transition. Nevertheless, both $E_g$ values agree well with corresponding literature: refs [30, 31, 136] for $E_g \sim 1.6 - 1.7$ eV assuming indirect allowed transition, and refs [137, 138] for $E_g \sim 2.5 - 2.7$ eV assuming direct allowed transition.

74
In this work, we used the former assumption of indirect-allowed transition because it falls in line with the theoretical calculated band structure [44].

![Graph showing (αhv)^m as a function of hv for VO_2 thin films with shown amount of Mg, with band gap energy E_g extracted by linear fit. (a) m = 1/2 assuming indirect allowed transition; (b) m = 2 assuming direct allowed transition.](image)

*Figure 5.13: (αhv)^m as a function of hv for VO_2 thin films with shown amount of Mg, with band gap energy E_g extracted by linear fit. (a) m = 1/2 assuming indirect allowed transition; (b) m = 2 assuming direct allowed transition.*

Apart from the above described method, an alternative method is available which allows the determination of the band gap without considering the nature of the transition [139]. It is not in the scope of this thesis, so I do not discuss it here.
6. Input data for Computation

6.1 VO₂ Spheroidal Nanoparticle Inclusions

In Sections 7.1 and 8.3 (reported in Papers I and VI), I consider a dilute suspension of solid VO₂ nanoparticles with spherical or ellipsoidal morphology embedded in a dielectric matrix and backed by a dielectric substrate, as in the structure shown in Fig. 4.1. The effective dielectric function $\varepsilon^{MG}$ of this structure is determined by using the Maxwell-Garnett theory as described in Chapter 4.2.1.1.

I consider the dielectric matrix to have optical properties similar to that of glass or polymer and the dielectric substrate to be glass-like. So the dielectric function for the dielectric matrix $\varepsilon_m$ and that of the substrate $\varepsilon_{sub}$ are set to be $\varepsilon_m = 2.25$ and $\varepsilon_{sub} = 2.25$.

The optical constants of VO₂ have been determined several times [29, 31, 47, 48, 137, 140, 142, 143] as well as in section 5.7.2. A selection of these literature values [47, 48, 137, 140, 142] are plotted together with those determined in in section 5.7.2 in Fig. 6.1. As one can see, they agree with each other fairly well apart from "Tazawa et al. 1998" [140], for $n$ in the semiconducting state.

For the calculations for results in 7.1, I used data determined by Mlyuka et al. in our group [48], based on a 50 nm thick film and shown in Fig. 5.7.2, whereas results in 8.3 were derived from $n$ and $k$ determined in section 5.7.2 (in Fig. 6.1 marked as "Mlyuka 2009" for Paper I and "Present work" for Paper IV and VI). VO₂ in the metallic state is shown to have an exceptionally small scattering time with $\hbar/\tau_f \approx 0.7$ eV [108, 144] and a very small Fermi velocity $v_F \approx 2.4 \times 10^5$ m/s [145]. This results in a very small mean free path, about the order of the lattice constant. VO₂ may not even be a conventional Fermi liquid [145]. An alternative work [146] suggests that the mean free path may be one order of magnitude larger, but not large enough to invoke particle size dependence. Following the discussion about particle size in Chapter 4.1.5, it is clear that the term $\frac{2v_F\tau_f}{D_p}$ is negligible, and hence it is appropriate to put $\varepsilon_p = \varepsilon_f$.

In addition, as input parameter for the Maxwell-Garnett theory, the filling factor of the VO₂ particles was fixed at 0.01. The thickness of the layer $d$ was set to be 5 $\mu$m (Section 7.1, 8.3) or to vary $0 < d < 20$ $\mu$m (Section 8.3.2), which are equivalent to a 50 nm thick VO₂ film or films with $0 < d < 200$ nm, respectively, in terms of the amount of VO₂. The cases for spheres, prolate
spheroids and oblate spheroids are characterized using the aspect ratio $m$ as also defined in Fig. 4.1.

Optical transmittance and reflectance for normal incidence onto such a composite layer backed by a substrate was calculated using the matrix formalism in standard thin film calculations based on Fresnel’s equations. Here we used the method that is introduced in Ref. [113] as described in Chapter 4.3.3. The optical transmittance and reflectance of VO$_2$ thin film with different thickness, varied from 0.01 $\mu$m to 0.1 $\mu$m was also calculated for comparison. The wavelength-integrated optical properties, luminous transmittance and solar transmittance were calculated using Eq. (2.7).

6.2 VO$_2$ Spherical Core-shell Nanoparticle Inclusions

In Chapter 7.2 and Paper II, calculations were done on spherical core-shell particles. The model considers a dilute suspension of VO$_2$ nanoparticle shells enclosing dielectric cores embedded in a glass or polymer-like dielectric medium and backed by a dielectric substrate. The structural model is shown in Fig. 4.2. The Maxwell-Garnett theory for core-shell nanoparticles,
described in Chapter 4.2.1.3, was used to determine the effective dielectric function $\varepsilon_{MG}$.

For the dielectric medium and the dielectric substrate I used the same input dielectric function value, i.e., $\varepsilon_{m} = \varepsilon_{sub} = 2.25$. The refractive index of the dielectric core $n_c$ was varied to represent different materials: 1 vacuum or air, 1.5 glass or polymer, 2 and 2.5 some common transparent high refractive index materials such as ZnO and TiO$_2$.

For the VO$_2$ particle shells, the same arguments as in Chapter 6.1 apply, so the dielectric function determined from a VO$_2$ film marked as "Mlyuka et al. 2009" shown in Fig. 6.1 was used as input dielectric function. For the same reason, the absolute value of $x$ and $t$ were not treated in the calculation in Eq. (4.36).

As input parameters for the Maxwell-Garnett theory, the composite layer was set to be 5 $\mu$m thick and the relative volume amount of VO$_2$ in the layer is kept 0.01 constant. The ratio between the diameter ($x$) of the spherical core and the thickness ($t$) of the shell $x/t$ was varied from 0 to 20, and accordingly the filling fraction of the particles $f$ goes from 0.01 to 0.04 as explained in Eq. (4.39).

Optical transmittance and reflectance for normal incidence onto the above mentioned composite layer backed with a substrate were calculated using the same method as described in Chapter 6.1. The wavelength-integrated optical properties, luminous transmittance and solar transmittance were calculated using Eq. 2.7. The solar transmittance modulation $\Delta T_{sol}$ was calculated using Eq. 3.1.

### 6.3 Composites of VO$_2$ and ITO

In Chapter 7.3 and Paper III, calculations were done on a composite layer of VO$_2$ and ITO. The model considers a random mixture of nanoparticles of VO$_2$ and ITO. The VO$_2$ and ITO units were taken to be spherical and topologically equivalent. The Bruggeman theory, described in Chapter 4.2.2, was used to determine the effective dielectric function $\varepsilon_{BR}$ of such a composite layer.

For the input dielectric function of VO$_2$, the same argument as in Chapter 6.1 stands; thus I used the dielectric function marked as "Mlyuka et al. 2009" shown in Fig. 6.1.

The dielectric function of ITO was determined for a 200 nm thick ITO film by Hamberg et al. [16], in which they derived the optical constants for ITO with different values of free electron carrier concentration $n_e$. We used the results from ITO with $n_e = 6.2 \times 10^{20}$ cm$^{-3}$, as shown in Fig 6.2. The free electron mean free path of a high-quality ITO is very short, $\sim 5$ nm, and is governed by ionized impurity scattering in the infrared. Considering the effect of particle size, discussed in Chapter 4.1.5, the situation is analogous to the one in VO$_2$ and it is clear that this effect can be ignored. Hence the
The optical constants in Fig. 6.2 were used as the input dielectric function for ITO particles. In these calculations, the ITO mass thickness was considered to be constant at 200 nm, while the VO_2 mass thickness varied so that the overall VO_2 volume fraction in the composite layer \( f \) ranged from 0.1 to 0.5.

Optical transmittance and reflectance for normal incidence onto the above mentioned composite layer backed with a substrate were calculated using the same method as described in Chapter 6.1. The wavelength-integrated optical properties, luminous transmittance, solar transmittance and the solar transmittance modulation \( \Delta T_{sol} \) were obtained using the same method as described in Chapter 6.2.
Part II:
Important Results

"In theory, there is no difference between theory and practice; In practice, there is."

a Yogi Berra quote spotted in book "Antifragile: Things That Gain From Disorder" by Nassim Taleb
7. Nanothermochromics with Undoped VO$_2$: Modeling Results

7.1 Dielectric Matrix with VO$_2$ Spheroidal Nanoparticle Inclusions

In this section, calculated results from a layer with a dilute suspension of VO$_2$ solid spheroidal nanoparticles in a dielectric matrix are shown. A comparison with the results for VO$_2$ films is made to show that VO$_2$ nanoparticle layers have very much improved luminous transmittance and solar transmittance modulation compared with VO$_2$ films.

7.1.1 VO$_2$ Films

![Figure 7.1: Computed spectral transmittance for VO$_2$ films in semiconducting (τ < $\tau_{cr}$) (a) and metallic (τ > $\tau_{cr}$) (b) states.](image)

Computed spectral transmittance of VO$_2$ films of different thicknesses are shown in Fig. 7.1. For both semiconducting and metallic states, $T(\lambda)$ decreases as the film thickness is increased. The low transmittance dominating the UV and a part of the visible range corresponds to the inter-band transition from the O 2$p$ to the $d$ band. For the semiconducting state (Fig. 7.1 (a)), $T(\lambda)$ increases at long wavelengths; in contrast, the transmittance for the metallic state peaks at $\sim$700 nm and goes down at long wavelengths, which marks the
characteristic near-infrared thermochromic switching for typical VO$_2$ films. The most efficient switching is located at $\sim$2500 nm.

Fig. 7.2 shows computed integrated properties (Eq. (2.7)), specifically luminous transmittance $T_{lum}$, solar transmittance $T_{sol}$ and solar transmittance modulation $\Delta T_{sol}$ derived from $T(\lambda, \tau)$ in Fig. 7.1. An increase of the film thickness can increase the solar transmittance modulation $\Delta T_{sol}$, as defined in Eq. (3.1), but also causes $T_{lum}$ to decrease to an undesirably low level. As a result, requiring a noticeable solar transmittance modulation $\Delta T_{sol}$ limits $T_{lum}$ to less than $\sim$ 40%. For a 50 nm thick VO$_2$ film, as one can pinpoint in Fig. 7.2, we have $T_{lum}(\tau < \tau_{cr}) \approx T_{lum}(\tau > \tau_{cr}) = 37.4\%$ and $\Delta T_{sol} = 6.5\%$.

![Figure 7.2: Computed luminous (a) and solar (b) transmittance and (c) solar transmittance modulation corresponding to data in Fig. 7.1 as a function of thickness of VO$_2$ films.](image)

7.1.2 VO$_2$ Nanoparticles vs. Film

Spectral transmittance, reflectance and integrated optical properties for a layer with a dilute suspension of VO$_2$ solid spheroidal nanoparticles in a dielectric matrix characterized with $\varepsilon_m = 2.25$ backed by a dielectric substrate with the
Figure 7.3: Computed spectral transmittance and reflectance for spheroidal VO$_2$ particles (as in Fig 4.1(a), (b) and (c)), with the shown aspect ratio $m$ and a filling factor of 0.01, dispersed in a dielectric medium. The spheroids have their symmetry axes perpendicular to the substrate. (a) and (c) refer to VO$_2$ in semiconducting state ($\tau < \tau_{cr}$), (b) and (d) refer to VO$_2$ in metallic state ($\tau > \tau_{cr}$).
Figure 7.4: Integrated luminous (a), solar (b) transmittance and (c) solar modulation corresponding to data in Fig. 7.3 for spheroidal VO\textsubscript{2} particles (as in Fig 4.1(a), (b) and (c)), with the shown aspect ratio $m$ and a filling factor of 0.01, dispersed in a dielectric medium. The spheroids have their symmetry axes perpendicular to the substrate.
same dielectric constant were computed. The layer thickness was taken to be 5 µm and the content of VO₂ particles was 1 vol.%; this is equivalent to a 50 nm thick VO₂ film (i.e., both contain the same amount of VO₂). Different spheroidal shapes, i.e., prolate spheres and oblate spheres, characterized with an aspect ratio \( m \) as defined in Fig. 4.1, are taken into consideration.

The spectral transmittance and reflectance for spheroids oriented with symmetry axes perpendicular to the substrate as depicted in Fig. 4.1 (a) (b) and (c) are shown in Fig. 7.3. The aspect ratio \( m \) is varied from 0.1 to 10. \( R(\lambda) \) of both semiconducting states and metallic states are low and mostly flat. \( T(\lambda) \) increases monotonically as \( m \) increases. The low transmittance dominating the UV and a part of the visible range is the result of the absorption due to inter-band transitions for O 2p to d band. The most salient feature in Fig. 7.3 is the pronounced absorption for the metallic state in the near-infrared, which is centered at \( \sim 1.2 \) µm for spheres, due to a heavily damped plasmon resonance in the metallic state of VO₂ [147]. This feature marks an efficient thermochromic switching, because the solar irradiance intensity is high in this wavelength range. The location of the absorption band goes to shorter wavelength for prolate spheroids and a longer wavelength for oblate spheroids. Moreover, \( T(\lambda) \) in the visible range is much higher than that of the VO₂ film.

Fig.7.4 shows the integrated properties \( T_{lum} \), \( T_{sol} \) and \( \Delta T_{sol} \) as obtained from the spectra in Fig. 7.3. The particle shape dependence is consistent with spectra in Fig. 7.3. \( T_{lum} \) increases monotonically as \( m \) increases. Particles with larger \( m \) offer much higher \( T_{lum} \) than that of a corresponding 50-nm-thick film ( \( T_{lum} = 37.4\% \)), while \( \Delta T_{sol} \) decreases somewhat but is still 2 ~ 3 times as large as that of a corresponding film (\( \Delta T_{sol} = 6.5\% \)). For the intermediate case of spheres (\( m = 1 \)), we have \( T_{lum} \) of 72% and 62% for the semiconducting and metallic states, respectively, and \( \Delta T_{sol} \) is 16.7%.

Randomly oriented spheroids are of interest as well. Spectral transmittance for VO₂ particles of different shapes is shown in Fig.7.5, and the integrated properties \( T_{lum} \) and \( \Delta T_{sol} \) are shown in Fig. 7.6. The same as in the case for oriented spheroids, both \( T_{lum} \) and \( \Delta T_{sol} \) are high, with a maximum of \( T_{lum} \) occurring for spheres (\( m = 1 \)) while \( T_{sol} \) is very much the same for all shapes (across all values of \( m \)).

The above computational results show that VO₂ particle based materials can offer greatly improved luminous transmittance and solar transmittance modulation compared to films. This makes VO₂-based thermochromic windows much more suitable for practical use in energy efficient applications.
Figure 7.5: Spectral transmittance for spheroidal VO$_2$ particles (as in Fig 4.1(d)), with the shown aspect ratio $m$ and a filling factor of 0.01, dispersed in a dielectric medium. The spheroids are randomly oriented. Parts (a) and (b) refer to VO$_2$ in semiconducting ($\tau < \tau_{cr}$) and metallic states ($\tau > \tau_{cr}$), respectively.

Figure 7.6: Integrated luminous (a), solar (b) transmittance and (c) solar modulation corresponding to data in Fig. 7.5 for spheroidal VO$_2$ particles (as in Fig. 4.1(d)), with the shown aspect ratio $m$ and a filling factor of 0.01, dispersed in a dielectric medium. The spheroids are randomly oriented.
7.2 Dielectric Matrix with VO\textsubscript{2} Core-shell Nanoparticle Inclusions

Spectral transmittance and reflectance were calculated for a composite layer with VO\textsubscript{2} shells enclosing a dielectric core characterized with \( n_c \) in a glass or polymer-like dielectric matrix with refractive index \( n_m = 1.5 \) backed by a glass-like dielectric substrate with refractive index \( n_{sub} = 1.5 \) as shown in the structural model in Fig. 4.2. As in Chapter 7.1, the amount of VO\textsubscript{2} was taken to be 1 vol.%, and the layer thickness was 5 \( \mu \)m, equivalent to a 50 nm thick film.

![Graphs showing spectral transmittance for different ratios of \( x/t \).](image)

*Figure 7.7: Spectral transmittance calculated for spherical shells (thickness \( t \)) of VO\textsubscript{2} enclosing cores (diameter \( x \)) with the shown values of the dielectric constant \( n_c \) and embedded in a dielectric medium represented by \( n_m = 1.5 \), as depicted in Fig. 4.2. Data are shown for \( \tau < \tau_{cr} \) (semiconducting VO\textsubscript{2}) (a) and (c) and for \( \tau > \tau_{cr} \) (metallic VO\textsubscript{2}) (b) and (d). The material was 5 \( \mu \)m thick and contained 1 vol. % of VO\textsubscript{2}.*

In Figure 7.7, spectral transmittance is presented for \( n_c = 1 \) and 2 for different ratios between the diameter \( x \) of the dielectric core and the thickness \( t \) of VO\textsubscript{2} shell, specifically for \( x/t \) being 0, 5, 10, 15, 20. At the semiconducting...
state ($\tau < \tau_{cr}$), the spectral shape is quite similar to the case of solid spheres in Chapter 7.2. $T(\lambda)$ drops with increasing $x/t$, with the case of $n_c = 1$ being most sensitive to $x/t$. The metallic state ($\tau > \tau_{cr}$) presents a striking feature: a valley that moves to the long wavelength region with increasing $x/t$, indicating an absorption as a result of a heavily damped plasmon resonance due to the conduction electrons in the metallic state of VO$_2$ [147]. The minimum of this valley, equivalent to the peak of the plasmon absorption, is shifted monotonically from $\sim 1.2$ $\mu$m for $x/t = 0$ to $\sim 2$ $\mu$m for $x/t = 20$. The valley is shallower when $n_c$ takes a larger value.

The integrated properties $T_{lum}$ and $T_{sol}$ for the semiconducting state and the metallic state and $\Delta T_{sol}$ are computed based on $T(\lambda)$ in Fig. 7.7 for cores with the refractive index being 1, 1.5, 2, 2.5, and $x/t$ is varied according to 0, 1, 2, ...20. Data in Fig. 7.8 show that $T_{lum}$ and $T_{sol}$ for both semiconducting state ($\tau < \tau_{cr}$) and metallic state ($\tau > \tau_{cr}$) decrease monotonically with increasing $x/t$. However, as $n_c$ increases, this effect tends to become weaker, with data lines for $n_c = 2.5$ being almost flat. The solar transmittance modulation $\Delta T_{sol}$ increases with decreasing $n_c$, with $n_c = 1$ (hollow spheres) having the maximum $\Delta T_{sol}$. The largest $\Delta T_{sol}$ is 20.9%, which occurs for $n_c = 1$ hollow spheres at $x/t \approx 10$ and is significantly higher than $\Delta T_{sol} \sim 16.7\%$ of VO$_2$ solid nanospheres. However, $T_{lum}$ for $\tau < \tau_{cr}$ at this point is compromised, and concomitantly decreased to $\sim 59\%$, i.e., a lower value than $73.5\%$ for VO$_2$ solid nanospheres.

The simultaneous gain in solar modulation and luminous transmittance requires more discussion since high values of both solar transmittance and luminous transmittance are desirable for most practical applications. It can be inferred from the above calculated results that the ideal case may lie at $x/t = 10$ for hollow spheres, so an additional computation for a number of VO$_2$ volume fractions with values smaller than 0.01 were done to extract this information. The results show that requiring $T_{lum}$ to be $\sim 73.5\%$ gives $\Delta T_{sol} \approx 14.5\%$ for hollow spheres with $x/t = 10$ with VO$_2$ volume fraction 0.005, i.e., 50% of the value used for the calculations in Fig. 7.7 and Fig. 7.8. With 60% of that amount (VO$_2$ volume fraction 0.006), one can achieve $T_{lum} \approx 70.5\%$ and $\Delta T_{sol} \approx 16.2\%$. These results, especially the latter, indicate a possibility of significantly decreasing the amount of VO$_2$ to achieve properties only marginally inferior to that of solid spheres, by using moderately thin-walled VO$_2$ hollow nanospheres.
Figure 7.8: Luminous transmittance (a) and (b), solar transmittance (c) and (d), and solar modulation (d) corresponding to data in Fig 7.7 for spherical shells (thickness $t$) of VO$_2$ surrounding cores (diameter $x$) with the shown values of the dielectric constant $n_c$ and embedded in a dielectric medium represented by $n_m = 1.5$, as depicted in Fig. 4.2. Data are shown for $\tau < \tau_{cr}$ (semiconducting VO$_2$) (a) and (c) and for $\tau > \tau_{cr}$ (metallic VO$_2$) (b) and (d). The material was 5 $\mu$m thick and contained 1 vol. % of VO$_2$. 
7.3 Composites of VO2 and ITO

The effective dielectric functions were derived from Bruggeman theory, as described in Section 6.3. Spectral transmittance \( T(\lambda) \) and reflectance \( R(\lambda) \) and integrated properties for both semiconducting state \((\tau < \tau_{cr})\) and metallic state \((\tau > \tau_{cr})\) were computed for VO2-ITO composite layers backed by a dielectric substrate with \( \varepsilon_{sub} = 2.25 \).

Fig. 7.9 shows \( T(\lambda) \) and \( R(\lambda) \) for VO2-ITO composite layers. The ITO mass thickness was kept constant at 200 nm while the VO2 volume fraction ranged from 0.1 to 0.5 for both \( \tau < \tau_{cr} \) and \( \tau > \tau_{cr} \). It can be seen that \( T(\lambda) \) has a higher value at 500 nm < \( \lambda < 1500 \) nm, and the thermochromic switching is also significant in this range. The most effective switching is centered around 1200 nm, which is consistent with previous computations on VO2 particles embedded in a dielectric matrix done in Chapter 7.1 and 7.2. \( R(\lambda) \) increases monotonically when the wavelength gets longer than 1000 nm and it reaches 60% at \( \lambda = 2500 \) nm. The spectral shape of \( T(\lambda) \) and \( R(\lambda) \) for low filling factors of VO2 preserve the characteristic features of a 200 nm thick ITO layer in a previous study [16], which yielded a low thermal emittance of \( E_{therm} \approx 0.2 \). The addition of VO2 will no doubt increase \( E_{therm} \), but for a small VO2 content \( E_{therm} \) should remain low and the composite film with low VO2 content can serve as a low-emittance coatings.

Fig. 7.10 shows integrated properties, specifically \( T_{lum}, T_{sol} \) and \( \Delta T_{sol} \) as a function of VO2 volume fraction. \( T_{lum} \) and \( T_{sol} \) are higher at \( \tau < \tau_{cr} \) than at \( \tau > \tau_{cr} \), which shows the presence of thermochromic switching. \( T_{lum} \) and \( T_{sol} \) decrease progressively as the VO2 amount is increased. The fact that both \( T_{lum} \) and \( T_{sol} \) follow the same trend indicates that the thermochromic switching is not localized in the near infrared but spreads out to the visible region as well. Fig. 7.10 shows \( \Delta T_{sol} \) as a function of the VO2 content. \( \Delta T_{sol} = 10\% \) occurs for \( f \approx 0.196 \), which simultaneously yields \( T_{lum} \approx 59.7\% \) for \( \tau < \tau_{cr} \). \( \Delta T_{sol} \) has a broad maximum of \( \sim 12.8\% \) around \( f \sim 0.35 \), where the VO2 units start to percolate in the Bruggeman model. These improvements on \( T_{lum} \) and \( \Delta T_{sol} \) show distinctive advantages over data for multilayer films reported recently for VO2 with a top layer of Pt [148] or ZnO:Al [149], the best of which, yielded modestly \( T_{lum} \approx 46\% \), \( T_{sol} \approx 4\% \) and \( E_{therm} \approx 0.3 \) [149].
Figure 7.9: Spectral transmittance (a) and reflectance (b) computed for ITO-VO$_2$ composites as discussed in the main text. The VO$_2$ volume fraction is denoted by $f$. Results are shown for $\tau < \tau_{cr}$ (semiconducting VO$_2$) and for $\tau > \tau_{cr}$ (metallic VO$_2$).
Figure 7.10: Wavelength-integrated luminous (a) and solar (b) transmittance corresponding to data in Fig. 7.9, and thermochromic modulation of the solar energy throughput (c), computed as a function of the VO$_2$ fraction $f$ for ITO-VO$_2$ composites. Results are shown for $\tau < \tau_{cr}$ (semiconducting VO$_2$) and for $\tau > \tau_{cr}$ (metallic VO$_2$). Circles indicate the data and connecting lines were drawn for convenience.
7.4 Summary

I have calculated the optical properties for layers containing suspensions of solid spheroidal VO$_2$ particles, VO$_2$ shells enclosing dielectric cores, and composites of VO$_2$ and ITO. The results have shown significantly enhanced $T_{lum}$ and $\Delta T_{sol}$ for VO$_2$ nanospheres embedded in dielectric layers, and results on VO$_2$ hollow spherical nanoshells have shown an even more improved $\Delta T_{sol}$ and a potential to lower the material costs. Moreover, results on composites of VO$_2$ and ITO have shown the possibility of combining low $E_{therm}$, high $\Delta T_{sol}$ and a moderately high $T_{lum}$ in one composite layer. VO$_2$ based nanothermochromics have certainly opened up new vistas for energy efficient window applications.
8. Mg-doped VO₂: Band gaps and Performance Limits

This chapter covers the experimental work done on Mg-doped VO₂ films, as well as optical properties of films and nanoparticles revealed by modeling. Section 8.1 covers the study reported in Paper V, which investigated the effect of Mg-doping on the band gaps of VO₂. Sections 8.2 and 8.3 correspond to the studies documented in Paper VI, which explores the performance limits of Mg-doped VO₂ films and nanoparticles derived from optical modeling results yielded from optical constants determined from experimentally prepared Mg-doped VO₂ films.

8.1 Band Gaps

Mg-doping offers lowered τ<sub>cr</sub>, higher luminous transmittance [36] via a lowered optical absorption in the visible and widened band gap [44]. A recent realization of nanothermochromics with Mg-doped VO₂ also suggests an additional benefit of bluish color [42]. However, we are not aware of any prior study that systematically and quantitatively addresses the effect of Mg-doping on the band gap widening, and felt the obligation to do so, hence the result of this work.

We have grown more than 45 samples of Mg-doped VO₂ thin films to a thickness of 40 < d < 87 nm. More than 38 of them were evaluated with RBS for elemental composition. The atom ratio Mg/(Mg+V) ≡ z was found to be 0 < z < 0.21. 11 samples showed a presence of Si content of 0.45 ± 0.07 at. % in the Mg-doped VO₂ layer, which was a result of the silicone adhesive from the high vacuum tape that was used in the deposition at the time. This contamination was later eliminated by equipping the substrate holder with metal clamps for sample-fixation. The rest of the samples have shown nothing but Mg-doping.

The optical measurements were done as described in 5.6, the optical constants were determined as discussed in 5.7. The Mg-doped samples were evaluated with the "surface+back" and "back" method. The (Mg, Si)-codoped samples were evaluated with surface method. The band gap values were collected from 38 samples in total following the methodology as described in 5.8. Band gaps were also extracted in the same way (see Section 5.8) from literature data on optical constants [47, 48, 137, 140, 142] for comparison.
The results were plotted as a function of atom ratio Mg/(Mg+V). The results of samples doped with only Mg are shown in Figs. 8.1 (a) and (b) for data obtained from the "surface+back" method and "back" method, respectively. For the Mg-doped VO\textsubscript{2} samples with Si contamination, the results are shown in 8.2. All of the data show a clear rising trend with increasing Mg content, and a linear dependency can be extracted as:

\[ E_g(z) = E_g(0) + \xi z \]  

with parameters \( E_g(0) \) and \( \xi \) shown in Table 8.1.

Table 8.1: Data for VO\textsubscript{2} films with shown dopants and with optical constants evaluated with "surface", "back" and "surface+back" methods. \( E_g(0) \) and \( z \) are the parameters in Eq.(8.1) acquired from linear fitting as described in the text.

<table>
<thead>
<tr>
<th>Doping</th>
<th>Evaluation method</th>
<th>( E_g(0) ) (eV)</th>
<th>( \xi ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>&quot;surface+back&quot;</td>
<td>1.65 ± 0.04</td>
<td>3.85 ± 0.44</td>
</tr>
<tr>
<td>Mg</td>
<td>&quot;back&quot;</td>
<td>1.80 ± 0.04</td>
<td>4.03 ± 0.39</td>
</tr>
<tr>
<td>Mg+Si</td>
<td>&quot;surface&quot;</td>
<td>1.68 ± 0.04</td>
<td>7.05 ± 0.85</td>
</tr>
</tbody>
</table>

Figure 8.1: Band gap as a function of atom ratio Mg/(Mg+V) for Mg-doped VO\textsubscript{2} films. Data were evaluated from optical constants obtained from \( R_s \), \( R_b \) and \( T \) using the "surfce+back" and "back" method. Literature data were obtained from optical constants determined by Verleur et al.[137], Tazawa et al.[140], Kakiuchida et al.[47], Mlyuka et al.[48], and Kana kana et al.[142]

Regarding the data from Mg-doped VO\textsubscript{2} films, 3 data points near \( z \sim 0.05 \) and 2 data points near \( z \sim 0.11 \) lie below the linear trend line in Fig. 8.1.
Figure 8.2: Band gap as a function of atom ratio Mg/(Mg+V) for (Mg, Si)-codoped VO$_2$ films with 0.45 ± 0.07 at.% of Si. Data were evaluated from optical constants obtained from $R_s$ and $T$ using the "surface" method. Literature data were obtained from optical constants determined by Verleur et al.[137], Tazawa et al.[140], Kakiuchida et al.[47], Mlyuka et al.[48], and Kana kana et al.[142]

(a) but on the line in Fig. 8.1 (b). These results were from the samples that were metallic as deposited and went through post-annealing, which might have caused sub-band-gap absorption. Despite the scattering of the data, the slope of the trend $\xi$ obtained from both the "surface+back" and "back" method were of a very similar value within each other’s statistical error, which adds to the reliability of our data.

The data from Mg-doped VO$_2$ films containing Si evaluated using the surface method in Fig. 8.2 show a stronger trend of band gap increase with Mg content $z$: the magnitude of $\xi$ is close to being doubled, showing a clear effect of Si as a "band gap enhancer". However, the data were only available for small amount of doping $z < 0.1$, and also due to the un-intended nature of the presence of Si, it is wise to be cautious and more systematic studies should be conducted in the future to confirm the effect of Si-doping on the band gap of VO$_2$.

In summary, this part of the study has shown the quantitative relation of Mg-doping on the band gap of VO$_2$ with thorough investigation conducted on a large number of samples. The band gap of VO$_2$ doped with only Mg was shown to increase by 3.9 ± 0.5 eV per unit atom ratio of Mg/(Mg+V) for 0<Mg/(Mg+V)<0.21. In addition, we have also found strong indications that the presence of a small amount of Si may enhance the band gap even more. These data shed light on the enhanced luminous transmittance (usually linked to a widened band gap) in Mg-doped VO$_2$ films and is a significant contribution to the knowledge and design parameters of energy-efficient thermochromic windows.
8.2 Modeling Results: Mg-doped VO$_2$ Thin Films

8.2.1 Films with Fixed Thickness 50 nm

Optical constants of experimentally prepared films were used as input data for the computation of spectral transmittance and reflectance for 50 nm thick films. The integrated properties $T_{lum}$ and $\Delta T_{sol}$ were calculated using Eq. (2.7) and (3.1). Fig.s 8.3 (a) and (b) show $T_{lum}$ as a function of Mg/(Mg+V) for the semiconducting state and metallic states, respectively. Both $T_{lum}$s increase with Mg content, consistent with the findings [44] that Mg-doping decreases the luminous absorptance. $\Delta T_{sol}$ as a function of Mg/(Mg+V) shown in Fig. 8.3(c) has a decreasing trend with Mg-doping.

Figure 8.3: Luminous transmittance $T_{lum}$ and solar energy transmittance modulation $\Delta T_{sol}$ as a function of Mg/(Mg+V) atom ratios for VO$_2$ films of 50 nm. $T_{lum}$ of semiconducting ($\tau < \tau_{cr}$) and metallic ($\tau > \tau_{cr}$) state are shown in (a) and (b), respectively. Data for solar modulation $\Delta T_{sol}$ are shown in (c).

These results indicates that the advantage of Mg-doping lies in the lowering of luminous absorptance. One has to search for a judicious choice of thickness
to allow the advantage of increased $T_{lum}$ to outweigh the disadvantage of decreased $\Delta T_{sol}$, and hence the study presented in the following section.

8.2.2 Performance Limits for One-layer Films

Spectral transmittance and reflectance were calculated for films with varied thicknesses in the range $0 < d < 200$ nm. Integrated properties $T_{lum}$ and $\Delta T_{sol}$ are computed for each Mg/(Mg+V) atom ratio and also for each thickness, and their relation is presented in Fig. 8.4. In this figure $T_{lum}$ is plotted versus $\Delta T_{sol}$, so that data with favorable total performances can be easily identified in the upper-right area of the figure. This plotting scheme gives a big advantage over Fig. 8.3, which shows fragmented performance only. In a sense, Fig. 8.4 can be viewed as a qualitative chart for the performance limit of Mg-doped VO$_2$ films. The evolution of data points from small to large $d$ values starts from the top-left corner and ends at the lower-right corner of the figure. The data are divided according to Mg/(Mg+V) $\equiv z$ atom ratio into 4 groups: $z = 0; 0 < z < 0.06; 0.06 < z < 0.11; 0.11 < z < 0.21$.

Samples with $0.11 < z < 0.21$ were "over-Mg-doped" and have bad performances, so they are not discussed. The rest of the samples all have the same trend with thickness: after an initial drop in relation to $d$, the data reaches a plateau region where the increase of thickness brings about increased $\Delta T_{sol}$ with almost unchanged $T_{lum}$. The key to good performance is to sustain a high $T_{lum}$ value before reaching this plateau, which is observed from most of the Mg-doped films; consequently, most of the data points from moderately Mg-doped films lie to the top-right to corresponding data from pure VO$_2$, suggesting a better performance than films of pure VO$_2$. For a target of $\Delta T_{sol} \sim 10\%$, one can achieve $T_{lum} \sim 45\%$ for the semiconducting state and a slightly lower value for the metallic state with Mg-doped films, whereas, undoped films only offer $T_{lum} \sim 30\%$ at the most.
Figure 8.4. $T_{\text{lum}}$ as a function of $\Delta T_{\text{sol}}$ for VO$_2$ films with shown Mg/(Mg+V) $\equiv z$ atom ratio. The film thickness was varied $0 < d < 200$ nm. Data were shown for semiconducting states ($\tau < \tau_{cr}$) (a) and metallic states ($\tau > \tau_{cr}$) (b).
8.2.3 Films with One-layer Antireflection Coatings

In this section, an attempt to improve $T_{lum}$ and $\Delta T_{sol}$ is made with computation assuming the application of one layer of antireflection (AR) coating with $n_{AR} = 1.5$ (typical of SiO$_2$ and many polymers) with thickness $0 < d_{AR} < 300$ nm on the top of the VO$_2$ films with Mg/(Mg+V) values and thickness $d$ values listed in Table 8.2, and results visualized in Fig. 8.5. Fig. 8.5 shows a trajectory with increasing $d_{AR}$ starting from the points marked with triangles with high-performance points marked with circles. It is clear that AR treatment can improve $T_{lum}$ by 8% in absolute value while increasing $\Delta T_{sol}$ by 2-3%. Well chosen parameters (bold numbers shown in Table 8.2), can offer $\Delta T_{sol} = 9.2\%$, with $T_{lum}(\tau < \tau_{cr}) = 59.3\%$ and $T_{lum}(\tau > \tau_{cr}) = 57\%$. Alternatively, one can and achieve $\Delta T_{sol} = 12.8\%$ and maintain $T_{lum}(\tau < \tau_{cr}) = 47.5\%$ and $T_{lum}(\tau > \tau_{cr}) = 44\%$; or $\Delta T_{sol} = 15.4\%$ with $T_{lum} \sim 30\%$. These highlighted performances are similar to the best performance of AR treatment of TiO$_2$/VO$_2$ reported by Chen et al. [45], who reported $\Delta T_{sol} \sim 15\%$ with $T_{lum}(\tau < \tau_{cr}) = 49.5\%$ and $T_{lum}(\tau > \tau_{cr}) = 45\%$.

![Figure 8.5: Luminous transmittance $T_{lum}$ as a function of solar energy modulation $\Delta T_{sol}$ for VO$_2$ films with shown Mg/(Mg+V) atom ratios and film thicknesses $d$. The curves form trajectories that evolve from $d_{AR} = 0$ marked with triangles and end at $d_{AR} = 300$ nm. Data are shown for the semiconducting state ($\tau < \tau_{cr}$) (a) and metallic state ($\tau > \tau_{cr}$) (b). Data points marked with circles are the high-performance points of each trajectory and are listed in Table 8.2.](image-url)
Table 8.2: Luminous transmittance $T_{lum}$ for the semiconducting state ($\tau < \tau_{cr}$) and metallic state ($\tau > \tau_{cr}$) and solar energy modulation $\Delta T_{sol}$ for Mg-doped VO$_2$ films with shown Mg contents and thickness $d$. Data are reported for before (numbers in brackets) and after the application of an antireflection coating. Parameters in bold are the high-performance points yielded by well-chosen parameters discussed in the text.

<table>
<thead>
<tr>
<th>Mg/(Mg+V)</th>
<th>$d$ (nm)</th>
<th>$d_{AR}$ (nm)</th>
<th>$\Delta T_{sol}$ (%)</th>
<th>$T_{lum}(\tau &lt; \tau_{cr})$ (%)</th>
<th>$T_{lum}(\tau &gt; \tau_{cr})$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>70</td>
<td>265</td>
<td>11.6 (8.4)</td>
<td>45.3 (35.1)</td>
<td>41.5 (32.8)</td>
</tr>
<tr>
<td>0.006</td>
<td>90</td>
<td>260</td>
<td>9.2 (7.3)</td>
<td>59.3 (50.7)</td>
<td>57 (49.7)</td>
</tr>
<tr>
<td>0.024</td>
<td>80</td>
<td>265</td>
<td>12.4 (9.3)</td>
<td>44.6 (36.6)</td>
<td>39 (31.6)</td>
</tr>
<tr>
<td>0.055</td>
<td>110</td>
<td>265</td>
<td>12.8 (10.4)</td>
<td>47.5 (42.5)</td>
<td>44 (39.4)</td>
</tr>
<tr>
<td>0.055</td>
<td>147.5</td>
<td>95</td>
<td>14.4 (12.3)</td>
<td>37 (30.2)</td>
<td>33.2 (29.7)</td>
</tr>
<tr>
<td>0.055</td>
<td>147.5</td>
<td>155</td>
<td>15.4 (12.3)</td>
<td>32.1 (30.2)</td>
<td>29.8 (29.7)</td>
</tr>
</tbody>
</table>
8.3 Modeling Results for Mg-doped VO$_2$ Nanospheres

8.3.1 5-µm-Thick Layer Containing 1 vol.% Nanospheres

The optical properties of Mg-doped VO$_2$ nanospheres were calculated using effective medium theory Maxwell-Garnett theory, as explained in section 4.2.1, which was also used for calculating results in section 7.1. The calculation assumes 1 vol.% Mg-doped VO$_2$ nanospheres distributed in a 5-µm-thick glass or polymer-like dielectric matrix with $n = 1.5$. The spectral transmittance and reflectance were calculated and the integrated properties $T_{lum}$ and $\Delta T_{sol}$ were calculated. In the section, VO$_2$ nanospheres are of equivalent amounts to that of films in Section 8.2.1 so that a comparison between nanoparticles and films can be made in parallel.

![Graphs showing $T_{lum}$ and $\Delta T_{sol}$ as a function of Mg/(Mg+V) atom ratios for 5-µm-thick nanocomposite layers containing 1 vol.% of VO$_2$. $T_{lum}$ for semiconducting ($\tau < \tau_{cr}$) and metallic ($\tau > \tau_{cr}$) states are shown in (a) and (b), respectively. Data for solar modulation $\Delta T_{sol}$ are shown in (c).](image)

Figure 8.6: Luminous transmittance $T_{lum}$ and solar transmittance modulation $\Delta T_{sol}$ as a function of Mg/(Mg+V) atom ratios for 5-µm-thick nanocomposite layers containing 1 vol.% of VO$_2$. $T_{lum}$ for semiconducting ($\tau < \tau_{cr}$) and metallic ($\tau > \tau_{cr}$) states are shown in (a) and (b), respectively. Data for solar modulation $\Delta T_{sol}$ are shown in (c).
The same as in Section 8.2.1, it can be seen in Fig.s 8.6 that $T_{lum}$ increases whereas $\Delta T_{sol}$ decreases with Mg content. By the same token as in 8.2.1, it is necessary to investigate optical properties with different thicknesses, as in the next section.

8.3.2 Performance Limits for Nanospheres

Luminous transmittance $T_{lum}$ for semiconducting ($\tau < \tau_{cr}$) and metallic state ($\tau > \tau_{cr}$) and solar transmittance modulation $\Delta T_{sol}$ for nanocomposites containing 1 vol.% Mg-doped VO$_2$ were computed for layer thicknesses $0 < d < 20$ µm. The results of $T_{lum}$ as a function of $\Delta T_{sol}$ in the same fashion as Fig. 8.4 are shown in Fig.8.7, with data divided into 4 groups: $z = 0$, $0 < z < 0.06$, $0.06 < z < 0.11$ and $0.11 < z < 0.21$. Fig.8.7 shows general trends of $T_{lum}$ as a function of $\Delta T_{sol}$, to some degree it can be viewed as a qualitative chart for performance limit of Mg-doped VO$_2$ nanoparticles. Specific data to compare pure and Mg-doped VO$_2$ are listed in Table 8.3.

It can be seen in Fig. 8.7 that in the form of nanospheres, pure VO$_2$ is the superior option. $\Delta T_{sol} = 10\%$ can be achieved with high luminous transmittance $T_{lum}(\tau < \tau_{cr}) \sim 82\%$ and $T_{lum}(\tau > \tau_{cr}) \sim 77.5\%$, the equivalent $T_{lum}$ for VO$_2$ films less than 35%. Furthermore, a large solar modulation $\Delta T_{sol} \sim 20\%$ (unattainable for films) can be achieved with $T_{lum}(\tau < \tau_{cr}) \sim 66\%$ and $T_{lum}(\tau > \tau_{cr}) \sim 57\%$. The reason for the advantage of undoped VO$_2$ nanoparticles can be explained by i) both undoped and the Mg-doped VO$_2$ have similar luminous absorption; ii) the positive effect on $T_{lum}$ seen in Mg-doped VO$_2$ films is absent in Mg-doped VO$_2$ nanoparticles; iii) the plasmon resonance in the NIR in the metallic states is stronger for the undoped VO$_2$ nanoparticles. The net effect of a large $\Delta T_{sol}$ in undoped VO$_2$ outweighs the increase of $T_{lum}$ offered by the Mg-doped VO$_2$ in nanoparticle composites.

Table 8.3: Luminous transmittance $T_{lum}$ for semiconducting state ($\tau < \tau_{cr}$) and metallic state ($\tau > \tau_{cr}$) and solar energy modulation $\Delta T_{sol}$ for nanocomposite layers containing 1 vol.% Mg-doped VO$_2$ with shown Mg contents and thickness $d$.

<table>
<thead>
<tr>
<th>Mg/(Mg+V)</th>
<th>$d$ (µm)</th>
<th>$\Delta T_{sol}$ (%)</th>
<th>$T_{lum}(\tau &lt; \tau_{cr})$ (%)</th>
<th>$T_{lum}(\tau &gt; \tau_{cr})$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>4.6</td>
<td>87.8</td>
<td>86</td>
</tr>
<tr>
<td>0</td>
<td>5</td>
<td>16.8</td>
<td>72.4</td>
<td>65.2</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>23.7</td>
<td>57</td>
<td>46.5</td>
</tr>
<tr>
<td>0.055</td>
<td>1</td>
<td>3.0</td>
<td>88.5</td>
<td>87.4</td>
</tr>
<tr>
<td>0.055</td>
<td>5</td>
<td>11.9</td>
<td>75</td>
<td>70.4</td>
</tr>
<tr>
<td>0.055</td>
<td>10</td>
<td>18.4</td>
<td>61.2</td>
<td>54</td>
</tr>
</tbody>
</table>

106
Figure 8.7: $T_{\text{lum}}$ as a function of $\Delta T_{\text{sol}}$ for nanocompomposite layers containing 1 vol.% VO$_2$ nanospherees with shown Mg/(Mg+V) atom ratios. Data are shown for semiconducting states ($\tau < \tau_{cr}$) (a) and metallic states ($\tau > \tau_{cr}$) (b).

8.4 Summary

This chapter reported our complete study on Mg-doped VO$_2$ for thermochromic window applications. Section 8.1 presented a linear relationship between the band gap and Mg-doping, which was found to increase by 3.9 ± 0.5 eV per unit atom ratio of Mg/(Mg+V) for 0<Mg/(Mg+V)<0.21. Si may be a potentially good additive to enhance this effect.
Section 8.2 and 8.3 dived further into the optical properties of Mg-doped VO$_2$ films and nanoparticle composite layers, by means of optical modeling. It was found that Mg-doped VO$_2$ films with Mg/(Mg+V) < 0.06 have much improved luminous transmittance and solar transmittance modulation. The performance can be further enhanced by applying one layer of antireflection coating on top of Mg-doped VO$_2$ films. On the other hand, the modeling results for nanocomposite films showed that the un-doped VO$_2$ is preferable. To include all the speculation on performance limits (joint performance of $T_{lum}$ and $\Delta T_{sol}$), Fig. 8.8 was constructed as a qualitative/approximate chart showing $T_{lum}$ as a function of $\Delta T_{sol}$ to be expected for undoped and Mg-doped VO$_2$ of various kinds, as shown. It should be noted that well-designed multilayer films [34, 48] can perform better than films with one-layer antireflection treatment, and that one-layer antireflection may also deliver exceptionally good results in some cases [45]. Nonetheless, simply by using a nanoparticle composite, one can effortlessly leap over a huge gap and achieve the *nanothermochromic* performance that is among the best of all.

**Figure 8.8:** Schematic illustration of approximate performance limits of VO$_2$ based materials for thermochromic energy efficient window applications. Data are shown for $T_{lum}$ in semiconducting state ($\tau < \tau_{cr}$) as a function of solar energy transmittance modulation $\Delta T_{sol}$ for undoped and Mg-doped VO$_2$ based materials: thin films, thin films with one-layer AR treatments and nanocomposite layers.
9. Sputter-deposited VO$_2$ Nanorods

This chapter covers the studies done in paper IV. In this study we grew VO$_2$ nanorods using DC magnetron sputtering and explored the growth parameters extensively and found out four factors that promoted rod-like growth of VO$_2$: substrate seeding, substrate temperature, O$_2$ gas flow, and thickness. The optical data showed enhanced absorptance and can be partially explained by optical modeling using the effective medium theory. A discussion on possible growth mechanisms was attempted.

9.1 Growth Conditions and Morphology

The fabrication of the VO$_2$ nanorods was described in Section 5.1.2. The important parameters are i) the O$_2$ flow varied as illustrated in Fig. 5.2 (a), (b) and (c); (ii) substrates, three kinds: glass, Au/glass and Au/SiO$_2$ nanopillars/glass; iii) The substrate temperature which was kept at either 450 °C or 550 °C and iv) thickness, varied $34 \leq d \leq 102$ nm.

The samples and corresponding growth conditions and their resultant morphology are listed in Table 9.1, with links to scanning electron micrographs Figs. 9.1, 9.2 and 9.3.
Figure 9.1: Scanning electron micrographs observed from the surface normal (top views) of the VO$_2$ samples 1-6 grown under the conditions described in Table 9.1. Note that the scale bar is different for samples 1-4 and samples 5-6.
Figure 9.2: Scanning electron micrographs for VO$_2$ samples 7-10 grown under the conditions described in Table 9.1. (a), (d), (g), (j) show top view; (b)(e)(h)(k) were taken $70^\circ$ off the surface normal of the samples; (c),(f), (i), (l) show cross section pictures.

Figure 9.3: (a) and (b) show scanning electron micrographs viewed from the cross section for VO$_2$ sample 11, grown under conditions described in Table 9.1 from a zoomed-out view and a zoomed-in view, respectively. (c) is a schematic illustration of sample 11.
Table 9.1: Fabrication parameters and morphology of the VO$_2$ samples. Samples in bold sample numbers were chosen for detailed analysis and optical modeling.

<table>
<thead>
<tr>
<th>ID No.</th>
<th>setup in Fig. 5.2</th>
<th>temperature ($^\circ$C)</th>
<th>substrate</th>
<th>mass thickness (nm)</th>
<th>morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a</td>
<td>450</td>
<td>glass</td>
<td>62.5</td>
<td>compact film Fig. 9.1 (a)</td>
</tr>
<tr>
<td>2</td>
<td>b</td>
<td>450</td>
<td>glass</td>
<td>62.5</td>
<td>rough film with grains Fig. 9.1 (b)</td>
</tr>
<tr>
<td>3</td>
<td>b</td>
<td>550</td>
<td>glass</td>
<td>34</td>
<td>small elongated grains Fig. 9.1 (c)</td>
</tr>
<tr>
<td>4</td>
<td>b</td>
<td>550</td>
<td>Au/glass</td>
<td>34</td>
<td>short rods Fig. 9.1(d)</td>
</tr>
<tr>
<td>5</td>
<td>b</td>
<td>550</td>
<td>glass</td>
<td>68</td>
<td>large elongated grains Fig. 9.1(e)</td>
</tr>
<tr>
<td>6</td>
<td>b</td>
<td>550</td>
<td>Au/glass</td>
<td>68</td>
<td>moderate rods Fig. 9.1(f)</td>
</tr>
<tr>
<td>7</td>
<td>c</td>
<td>550</td>
<td>glass</td>
<td>68</td>
<td>short rods Fig. 9.1 Fig. 9.2(a)-(c)</td>
</tr>
<tr>
<td>8</td>
<td>c</td>
<td>550</td>
<td>Au/glass</td>
<td>68</td>
<td>occasional long rods Fig. 9.2(d)-(f)</td>
</tr>
<tr>
<td>9</td>
<td>c</td>
<td>550</td>
<td>glass</td>
<td>102</td>
<td>dense long rods Fig. 9.2(g)-(i)</td>
</tr>
<tr>
<td>10</td>
<td>c</td>
<td>550</td>
<td>Au/glass</td>
<td>102</td>
<td>long rods and long wires Fig. 9.2(j)-(l)</td>
</tr>
<tr>
<td>11</td>
<td>a</td>
<td>450</td>
<td>Au/SiO$_2$ nanopillars/glass</td>
<td>34</td>
<td>long wires Fig. 9.3</td>
</tr>
</tbody>
</table>
9.1.1 Influence of O\textsubscript{2} gas flow

SEM micrographs of samples 1 and 2 are Fig.s 9.1 (a) and (b). Both are deposited at the same temperature and same thickness on the same substrate, but sample 2, grown with setup Fig. 5.2 (b), has much larger grains compared to sample 1, grown with Fig. 5.2 (a).

SEM micrographs of samples 5 is shown in Fig. 9.1 (e) and sample 7 in Fig. 9.2(a)-(c). With otherwise the same growth conditions, sample 7, grown with setup in Fig. 5.2 (c), has much more distinct rod-like growth.

To sum up, the effectiveness of setups into promoting large grains and rod-like growth can be ranked:

Fig.s 5.2 (c) > Fig.s 5.2 (b) > Fig.s 5.2 (a).

9.1.2 Influence of Substrates

The effect of substrate can be observed by comparing sample pairs, namely, samples 5 and 6 (Figs . 9.1 (e) and (f)); samples 7 and 8 (Fig.s 9.2(a)-(c) and (d)-(f)); samples 9 and 10 (Fig.s 9.2(g)-(i) and (j)-(l)). Within each pair, the conditions are the same, apart from the substrate being either glass or Au/glass. Samples 6, 8 and 10 grown on Au/glass has show much more distinct rod-like features than their counterpart samples 5, 7, 9 grown on glass substrates.

In addition, it is interesting to compare samples 11 with the rest of the samples. The detailed template Au/SiO\textsubscript{2} nanopillars/glass substrate have triggered the most salient nanowire growth, with length in \(\mu\)m order at substrate temperature 450 °C, with quite small thickness compared to other rod-like samples, (with only half the thickness of samples 5-8 and one third that of samples 9 and 10).

To rank the effectivity of substrates on promoting rod-like growth:

Au/SiO\textsubscript{2} nanopillars/glass > Au/glass > glass.

9.1.3 Influence of Substrate Temperature

Samples 2 and 5 are shown in SEM micrographs Fig.s 9.1 (b) and (e). Both are of similar thickness with the same growth parameters apart from the substrate temperature. Sample 5, grown at 550 °C, has much larger and more elongated grains than sample 2, grown at 450 °C.

One can conclude that to grow nanorods, the 550 °C is better than 450 °C.

9.1.4 Influence of Thickness

To clarify the influence of thickness, it is convenient to divide samples into 4 groups: A) samples 3 (Fig.s 9.1 (c)) and 5 (Fig.s 9.1 (e)); B) samples 7 (Fig.s 9.2 (a)-(c)) and 9 (Fig.s 9.2 (g)-(i)); C) samples 4 (Fig. 9.1 (d)) and 6 (Fig. 9.1

113
samples 8 (Fig.s 9.2 (c)-(f)) and 10 (Fig.s 9.2 (j)-(l)). Within each of these groups, the only differing parameter is thickness, and it can be seen that the thicker the sample the more rod-like growth it exhibits.

9.2 Optical Data and Modeling

9.2.1 Experimental Optical Data

The total and diffuse spectral transmittance and reflectance for samples 1, 2, 7 and 9 were recorded with a Lambda 900 instrument (Section 5.6) in $300 < \lambda < 2500$ nm, and were subjected to detailed optical analysis. The experimentally recorded total and diffuse spectral transmittance and reflectance are shown in Fig.s 9.4 and 9.5, respectively; and absorptance in Fig. 9.6 (a). It can be seen that rod-like samples 7 and 9 scatter light significantly more. In addition, the absorptance data for samples 7 and 9 are increased in the range $300 < \lambda < 1500$ nm for the semiconducting state, and shifted upwards in the entire measured spectral range for the metallic state, whereas the absorptance of samples 1 and 2 is lower and almost identical. Optical modeling with the effective medium theory was applied to offer a partial explanation for this enhanced absorption, which is not seen in sample 1 and 2 but present in samples 7 and 9.

9.2.2 Optical Modeling

Optical constants $n$ and $k$ were extracted from thin film sample 1 and were used as input data for analysis using the effective medium theory. For these samples we used the Bruggeman theory for randomly oriented spheroids (Eq. (4.41) and (4.42)) to model the optical properties of the rod-like films, as described in Section 4.2.2. For the model parameters we relied on close examination of the SEM pictures, which yielded roughly the parameters and suggested a model containing a dilute top layer with VO$_2$ particles with aspect ratio $m_t$, filling factor $f_t$ and thickness $d_t$ and a dense bottom layer with corresponding parameters $m_b$, $f_b$, $d_b$ satisfying:

$$d = f_t d_t + f_b d_b$$ (9.1)

where $d$ is the mass thickness as tabulated in Table 9.2. More detailed numbers were estimated by fine tuning the parameters to match spectral transmittance and reflectance. The parameters are shown in Table 9.2.

The spectral absorptance yielded by the optical modeling is shown in Fig. 9.6 (b). The modeled data (Fig. 9.6 (b)) show the same trend as the experimental data (Fig. 9.6 (a)) in the metallic state; samples 1 and 2 have relatively lower and almost identical absorptance. In contrast, samples 7 and 9 have an
upward shift in the modeled spectral range, especially that in the range 1000 < \( \lambda \) < 2500 nm agrees very well with the experimental data. In the semiconducting state, the modeling data represent very well samples 1 and 2, but show less absorptance for nanorod samples 7 and 9 compared with the experimental data. This effect maybe caused by the presence of defects such as excess of oxygen that is very likely to form at high deposition temperature. Multiple light-scattering in the nanorod samples is another possible cause for this enhanced absorption.

Figure 9.4: Experimental spectral total transmittance (a) and reflectance (b) for VO\(_2\) samples tabulated in Table 9.1. Data are shown for semiconducting states and metallic states.

9.3 Possible Growth Mechanism
The growth mechanism is unclear, but may be similar to high-temperature glancing-angle deposition (HT-GLAD) [150–154], which induces nanowire growth in metals when the substrate temperature is higher than around one third of the metal’s melting point and typically at a high deposition angle of \( \sim 80^\circ \) off the surface normal. In this study, it was found that significant rod-like
Figure 9.5: Diffuse transmittance $T_d$ and reflectance $R_d$ recorded for VO$_2$ samples tabulated in Table 9.1.

Figure 9.6: Spectral absorptance for VO$_2$ samples in semiconducting and metallic states. (a) shows experimental data for samples tabulated in Table 9.1; (b) shows the results from theoretical modeling using model parameters given in Table 9.2
Table 9.2: Optical models for samples No. 1, 2, 7, 9.

<table>
<thead>
<tr>
<th>sample/model</th>
<th>$d_i$</th>
<th>$f_i$</th>
<th>$m_i$</th>
<th>$d_b$</th>
<th>$f_b$</th>
<th>$m_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>62.5</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>70</td>
<td>0.893</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>125</td>
<td>0.05</td>
<td>3</td>
<td>125</td>
<td>0.494</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>500</td>
<td>0.01</td>
<td>10</td>
<td>200</td>
<td>0.485</td>
<td>10</td>
</tr>
</tbody>
</table>

growth can be attributed to the oxygen gas geometry which is related to particle flux of vanadium and oxygen. The rod-like growth induced by gold seeds maybe related to well-known gold-catalyzed vapor-liquid-solid growth mode [155] that is well-established for growing semiconductor nanowires.
10. Concluding Remarks and Outlook

In Chapter 7 it was shown by computation that nanothermochromics, i.e., thermochromic material consisting of VO$_2$ nanoparticle composites, can provide a promising solution to long sought-after VO$_2$-based thermochromic materials for energy-efficient fenestration. By using nanothermochromics, luminous transmittance $T_{lum}$ and the modulation of solar energy throughput between semiconducting state ($\tau < \tau_{cr}$) and the metallic state ($\tau > \tau_{cr}$) $\Delta T_{sol}$ can be increased to several times that of conventional thermochromic materials based on thin films. Core-shell nanoparticles were shown by calculation to increase $\Delta T_{sol}$ and produce a good performance with less material. The optical properties of ITO and VO$_2$ composites were revealed by computation to possess both low-emittance and good thermochromism.

Chapter 8 reports works done on Mg-doped VO$_2$. Experimental work was carried out on Mg-doped VO$_2$ films. Optical analysis based on absorption measurements showed that a quantitative relation between the larger band gap of VO$_2$ and Mg content can be established: the band gap of VO$_2$ increases by $3.9\pm0.5$ eV per unit atom ratio of Mg/(Mg+V) for $0<\text{Mg/(Mg+V)}<0.21$. A wider band gap has the advantage of moving the absorption out of the visible region thereby increasing the visible transmittance. Optical modeling, using the optical constants extracted from undoped and Mg-doped VO$_2$ films, was done to estimate the optical properties and performance limits of Mg-doped films and nanoparticles. It was found that the Mg-doped films, especially those moderately doped with $0<\text{Mg/(Mg+V)}<0.06$, are superior to those un-doped and the performance of Mg-doped films can be further boosted with one layer of antireflection coatings with a refractive index of $n = 1.5$. Calculation results on nanoparticle composites point to the un-doped VO$_2$ nanoparticles being a more favorable option to the Mg-doped ones. The best illustration to describe the studies on the thermochromic performance of VO$_2$ films and nanoparticles is presented in Fig. 8.8, with VO$_2$ based nanothermochromics as the best choice.

Another experimental study was done on the growth of VO$_2$ nanorods, reported in Chapter 9. The type of substrates, temperature of substrates during deposition, the thickness and the geometry of the oxygen gas inlet were identified as important factors that influence the morphology. Optical modeling of such particles was done and have shown good agreement between the experimental and simulated optical absorption. Further studies on this subject
are on-going in collaboration with Kyoko Namura and Prof. Suzuki from the Kyoto University group.

In the future, more synthesis and characterization of an integration of materials combining VO$_2$ nanocomposites and other functional materials such as ITO, electrochromic layers, solar cells or materials similar to "solar energy scavenging layers" [156] etc. should be done to achieve maximum energy efficiency. Future energy-efficient buildings could be extensively utilizing a clever combination of chromogenic smart windows accompanied by low-emittance or solar control coatings [7], photocatalytic paints for indoor air-cleaning [157], solar absorbers [158, 159], coatings with radiative cooling properties for cooling [160] and water condensation [161] as well as photovoltaics.

As to the "outlook" further into the future, I would like to divert from the so far rather "dry" narrative on VO$_2$ and "dream" a little. Nanomaterials are of great relevance to energy efficiency [11, 157, 162] owing to their small size, large surface area, great chemical reactivity and mechanical strength [163]. They will become essential constituents in future devices for lighting [164–166], detection/sensing [167–171], solar cells [167, 172–174], smart windows [175, 176], solar absorbers [158], catalysts [177, 178], photocatalysts [179, 180], batteries [181, 182], drug delivery [183, 184], cancer therapy [185, 186], and mechanical/structural applications [187–189], etc. For true energy-efficiency, future mankind will need to borrow much from nature’s mighty ability to "make order out of randomness" to ensure that design, synthesis, process, end-product and recycling are done with ease and generate little or no waste. Future material scientists will unleash the power of nature’s living factories, i.e., microorganisms such as bacteria and fungi, for the synthesis of materials, especially nanomaterials. Despite the infancy of the field, there is already a sizable achievement in synthesizing nanoparticles of metal [190–194], metal oxides [195], sulfides [191, 196, 197], SiO$_x$ [197], magnetic iron-based materials [198], ferroelectric materials [199], etc. In addition, materials of algal [200] and viral [201] origin can serve as batteries themselves. Let us not forget the ancient biogenic material -silk, which has newly discovered potential as a biodegradable building block for flexible electronic displays, tissue repairs, implantable optical systems and drug delivery, etc.[202]. On a macroscopic scale, future mankind will take more biomimetic approaches [203] and adapt the concept of "cradle-to-cradle design" [204] to make sure that the flow of energy and materials resembles that of cycles in a naturally self-sustaining ecosystem, and that nothing goes to waste. This is how I envision the future.
I Kapitel 7 förklaras, med hjälp av beräkningar, att termokroma material tillverkade av VO$_2$ nanopartiklar är mycket lovande VO$_2$-baserade kompositmaterial för energieffektiva fönster. Dessa material, s.k. nanotermokroma material (nanothermochromics), kan öka transmittansen av det synliga ljuset och i hög grad öka möjligheten att reglera transmittansen av nära infraröda våglängder (genom att variera temperaturen så att materialet går mellan halvledartillståndet ($\tau < \tau_{cr}$) och det metalliska tillståndet ($\tau > \tau_{cr}$), jämfört med traditionella termokroma material tillverkade av tunna filmer. Beräkningar visade även att nanopartiklar av VO$_2$, med skal av ett annat material, gör att reglering av solljuset kan åstadkommas med mindre mängd använt material. I detta kapitel beskrivs också hur de optiska egenskaperna hos kompositer av ITO och VO$_2$ beräknades, för att visa möjligheten att utveckla både lågemitterande och termokroma skikt.

Kapitel 8 beskriver det experimentella och teoretiska arbetet med Mg-dopad VO$_2$. Optiska analyser av resultat från absorptionsmätningar på dessa filmer visade på en tydlig relation mellan ökat bandgap hos VO$_2$ och mängden tillsatt Mg – bandgapet hos VO$_2$ ökar med 3.9 ± 0.5 eV per enhet av kvoten Mg/(Mg+V), för dopningskoncentrationer i området 0 < Mg/(Mg+V) < 0.2. Fördelen med ett ökat bandgap är att absorptionen förskjuts till kortare våglängder och ger ökad transmittans i det synliga våglängdsområdet. Optiska konstanter för odopade och Mg-dopade VO$_2$ filmer användes i optiska simulerings och gav teoretiska optiska egenskaper för dessa Mg-dopade filmer och kompositer innehållande nanopartiklar av VO$_2$. Resultaten visade att Mg-dopade filmer, speciellt vid låga dopningskoncentrationer 0 < Mg/(Mg+V) < 0.06, hade mycket bättre egenskaper än odopade filmer. Resultaten visade även att de optiska egenskaperna för Mg-dopade filmer kan förbättras ytterligare genom att belägga dem med ett antireflektierande skikt med brytningsindex n = 1.5. Däremot visade beräkningarna att kompositer med odopade VO$_2$ nanopartiklar hade bättre optiska egenskaper än då nanopartiklarna var Mg-dopade, vilket är illustrerat i Fig. 8.8. Experimentella studier av tillväxten hos nanostavar av VO$_2$ utfördes också, vilket presenteras i kapitel 9. Studien visade att substrat, mängd av deponerat material, substrattemperatur vid deponering och placering av ventiler för syrgas var faktorer som påverkade strukturen på dessa nanostavar. Fortsatta studier inom detta område är ett
fortgående samarbete med Kyoko Namura och Prof. Suzuki vid Kyoto universitet.

Inför framtiden är fortsatt syntetisering och karaktärisering av material av stor vikt för kommande förbättringar av energieffektivisering. Speciellt intressanta förbättringar kan åstadkommas om VO₂ nanokompositer kombineras med andra funktionella material, såsom ITO, elektrokroma tunna film, solceller och andra material där solenergi kan utnyttjas [155]. Det skulle t.ex. vara mycket lovande om framtida energieffektiva byggnader hade kombinationer av elektrokroma ”smarta fönster” och lågemitterande eller solkontroll skikt [7], fotokatalytisk inomhusfärgr för luftrening [156], solfångare [157,158], beläggningar med kylfunktion [159] och för kondensation av vatten [160], samt solceller.

Vidare vill jag gärna tillåta mig att ”drömma mig bort lite” och fundera på energi- och miljöfrågor i ett större sammanhang och på möjliga framtidsscenarier. Nanomaterial är - tack vare deras småskalighet, stora andel yta, utmärkta kemiska reaktionsförmåga och mekaniska tålighet [162] - mycket användbara inom många applikationer för energieffektivisering [11,156,161], t.ex. i belysning [163-165], sensorer [166-170], solceller [166,171-173], elektrokroma ”smarta” fönster [174,175], solfångare [157], katalys [176,177], fotokatalys [178-179], batterier [180-181], målinriktad läkemedelsleverans [182,183], cancerbehandling [184,185] och mekaniska/strukturrella applikationer [186-188], o.s.v. I framtiden är det troligt att faktisk energieffektivisering kommer att innebära att vi måste efterara naturens förmåga att ”skapa struktur från oordning”, och på så sätt försäkra oss om att utformning, syntes, process, slutprodukt och återvinning blir så optimera som möjligt och ger en minimal mängd restprodukter. Materialforskare borde i framtiden frigöra kraften i naturens livsväv, d.v.s. mikroorganismer som bakterier och svampar, för syntetisering av material, speciellt nanomaterial. Trots att arbetet inom detta område bara har börjat, har stora framsteg redan gjorts inom syntetisering av metallnanopartiklar [189-193], metalloxider [194], sulfider [190,195,196], SiOₓ [196], magnetiska järnbaserade material [197], ferroelektriska material [198], osv. Dessutom har alger [199] och virus [200] visats kunna fungera som batterier. Låt oss även påminna oss om det ypperliga biogena materialet silke, som nyigen visats vara mycket användbart som komposterbara byggestenar för böjbara elektriska skärmar, cellreparationer, implantbara optiska system och målinriktad läkemedelsleverans, o.s.v. [201]. På en makroskopisk skala borde människor i framtiden ha ett mer biomimetiskt förhållningssätt [202] och utnyttja ”cradle-to-cradle” utformningar [203] och på så sätt försäkra sig om att energi och livscykel ger ett självfungerande ekosystem utan restprodukter, på samma sätt som naturens egen livscykel. Det är så jag vill och hoppas att framtiden ska bli.
Acknowledgements

First and foremost I would like to thank my supervisor, Professor Claes-Göran Granqvist, the head of the Division of Solid State Physics, for offering me the opportunity to join this prestigious group. Thank you for being a visionary leader, opening my eyes with your innovative ideas, your guidance, readiness to help and for being so kind as to allow me to pursue my own ideas which can sometimes be a bit crazy. Your trust has empowered me and has given me a lot of confidence. I am very grateful for the "status of a panda" that you allowed me to have during the last month of writing.

I would also like to thank Professor Gunnar Niklasson, my co-supervisor, for your encyclopedic knowledge, your devotion to quality, your patience and for giving detailed answers for all my academic questions, big or small, and for encouraging me to dig deeper into the theoretical side of my research. I greatly appreciate your purity and peace of mind, and your rigor when it comes to scientific pursuit as well as to your passion for teaching.

During these years, I am very fortunate to have collaborated with brilliant scientists: Kyoko Namura and Professor Motofumi Suzuki from the Department of Micro Engineering are gratefully acknowledged for collaboration work done on sputter-deposited VO$_2$ nanorods. Many thanks to Professors Daniel Primetshofer and Göran Possnert from the Department of Physics and Astronomy, Uppsala University, Professor Anders Hallén from KTH-ICT, Royal Institute of Technology, Stockholm and Per Petersson from the School of Electrical Engineering, Fusion Plasma Physics, KTH Royal Institute of Technology, Stockholm for years of kind help with RBS measurements and analysis of my Mg-doped VO$_2$ samples. Nuru R. Mlyuka from the Department of Physics, University of Dar es Salaam, Tanzania is thanked for offering helpful tips about the deposition of VO$_2$, as well as providing samples and data for work done on band gaps of Mg-doped VO$_2$. Shuanglin Hu and Professor Kersti Hermansson from the Department of Chemistry, Uppsala University, Professors Rajeev Ahuja and Ralph Scheicher from Department of Physics and Astronomy, Uppsala University are thanked for the DFT hybrid functional calculations and brilliant input in the collaboration work on Mg-doped VO$_2$. Ilknur Pehlivan from the Division of Solid State Physics in the Department of Engineering Sciences at Uppsala University, Professor Delia Milliron and Evan Runnerstrom in the Lawrence Berkley National Laboratory are thanked for collaboration work done on ITO-polymer nanocomposite materials. K. Laaksonen, T. Ala-Nissila and R. M. Nieminen from the De-
partment of Applied Physics and COMP CoE, Aalto University School of Science, Finland and S. R. Puisto from MatOx Oy, Erottajankatu Helsinki, Finland are thanked for collaboration work done on a comparison between effective medium theory and four-flux theory.

I would like to express my gratitude for all the expertise Shuxi Zhao have offered on the sputter unit, optical measurements and optical analysis. Your old construction of a toroidal gas inlet played an important role in my Paper IV, and I am looking forward to seeing what the "showerhead" gas inlet is capable of. Your kind personality and care for others warms my heart, and I always enjoy your company. Thanks to Andreas Mattsson for your selfless help on many practical matters regarding equipments and so many other things (rice-transport etc). You keep absolutely 5-star (5 out of 5) standard in everything you do apart from your holidays, -since you have chosen not to rest but to "stand by" at home as our "helpdesk hotline", most of the time.

Thanks to Professor Arne Roos, for being a great teacher, sharing your excellent knowledge on optical setups, measurements and analysis. It is always delightful to talk to you, and your detailed explanation and demonstration have enabled me to improve the accuracy of my measurements and helped me to establish a solid foundation of knowledge in my head. Many thanks to Bobbie Roos for your kind and timely help with the English language and lovely British accent. Thanks to Professor Emeritus Carl-Gustaf Ribbing, Professor Mats Boman, Professor Emeritus Sten-Erik Lindquist and Professor Lars Österlund for readily sharing your knowledge, opinions, interesting stories and especially thanks to Professor C-G. R. for delicious apple-related products and Professor Mats B. for chocolates, -they are very nurturing to the brain. I am grateful to Professor Laszlo Kish for warm encouragement and fast-paced conversation full of wisdom and gems of physics. Thanks to Bengt Göteson for constructing a generally good infrastructure and warm atmosphere in the whole division, taking care of equipment, coffee, fruit and capturing lovely moments (including my portrait photo on the back cover of this thesis) with your beautiful photographic skills and sharing your nice photos. Many thanks to Maria Skoglund, Ingrid Ringärd, Sebastian Alonso, Inger Ekberg, Maria Melin, Anja Hohmann and Ylva Johansson for keeping many of the practical matters moving smoothly and in good order. Thanks to Enrique Carrasco and Jonatan Bagge for help with computers and software installations.

I am grateful to be in the same group with so many fun, helpful and inspiring colleagues. Pia Lansåker, Malin Johansson, José Montero Amenedo, Yuxia Ji, Ilknur Pehlivan and Sara Green, you are such great "multifunctional" peers, giving me so much from serious consultancy to great fun laughing loud together! Pia L. is gratefully acknowledged for kindly providing excellent Swedish summaries and help with RBS measurements. Annica Nilsson, thank you so much for being helpful and an excellent role model, not to mention your other qualities as the one who survived cycling from Uppsala to

124
Istanbul (yes, that one in Turkey!) and a talented silver smith. Anna-Malou Petersson, my cool competitive athletic mountain/ice-climbing adrenaline-junkie roommate/friend, your many adventure stories have enriched my life and all the best to your new conquests. Delphine Lebrun is appreciated for strong ideals, organizing skills, quality fika cakes and topics, boundless artistic imagination and the warm bonding that you have created in the department. Thanks to Miguel Arvizu for adding depth and sophistication to lunch table discussions. Professor Ewa Wäckelgård is appreciated for being cool, graceful, clear-minded and an admirable female role model in academia. Ruitao Wen and Yajun Wei are thanked for being the information hub and updating me about many events. Carlos Triana, your hard working spirit reminds me how diligent and passionate one can be toward physics. Magnus Wikberg is appreciated for funny and diverse conversation, sharing information and facts about the Netherlands and care for environmental issues. Christopher Maghanga, Maxwell Mageto, Stella Kioko, thank you for sharing really interesting stories, jokes and giving me useful tips about how to avoid leopards. Bozhidar Stefanov, Mikael Andersson, Anil Kumar Puri, Malin J., Matthias Hudl, Delphine L., Esat Pehlivan, Fang Mao, Roland Mathieu, Zareh Topalian, Iryna Valyukh, Wei Xia, Ruitao W., Umut Cindemir, David Lingfors, Joakim Munkhammar, Joakim Widén, Christopher Lundgren, Tarja Volotinen and Magnus Aberg are acknowledged for offering generous or even life-saving help. Zareh Topalian and Serkan Akansel are appreciated for contagious smily faces. Bozhidar S, thank you for sharing your insights about XRD, molecular cooking and so many interesting and diverse topics in chemistry. Anil K. P., Mikael A., Roland M., Umut C. and Serkan A. thank you for all the teasing, funny stories and witty conversations; the last month of writing was unexpectedly fun. Also appreciated was the rather early "magnetism 7.30 am. fika" with a historical touch from Professor Per Nordblad, and a hint of Russia from Professor Sergey Ivanov. Mattias Strömberg is thanked for his relaxing appearance and sharing really strong coffee. Rebecca Bejhed and Sofia Kontos are appreciated for adding glitter and color to the department. Professors Peter Svedlindh and Klas Gunnarsson are thanked for being good-humored. I am grateful for meeting so many other nice people who have visited this department, for short or long periods of time. Special thanks to José’s parents, José Montero and M. Carmen Amenedo for the beautiful 100+ years old artisan nail, which I have marveled, treasured from the first day, and will feel very regretful to part with. (Maybe I will keep it as a "timepiece" for decoration instead of using it to nail the thesis)

I would like to express my gratitude to all the people I have met in Kyoto, Japan, you are such a diverse, sophisticated and enriching crowd. Thanks to Kyoko Namura, your diligence, creative ways and delightful chats inspired me and revived many of the beautiful memories of my old days spent in Kyoto. Professor Motofumi Suzuki, I am grateful for your teaching (which some-
times resembles a fierce scolding but nevertheless is delightful in hindsight) about many practical experimental skills, and I will always remember your rule number one, to "think and use common sense instead of blindly executing manuals" and many many other principles that are nonexistent in textbooks. Professor Kimura Kenji is thanked for being very kind, patient, overwhelmingly brilliant and offering instant and mathematically non-trivial answers to my questions regarding theoretical matters. I am grateful for "Kimura lab seminar" and its organizers Profs. Kimura sensei, Suzuki sensei and Kaoru Nakajima sensei, for showing me the rigorous beauty of physics and that some knowledge and skills can only be acquired by digging deep the hard way. Hamachi Kenji is gratefully acknowledged for being helpful, a great role model and a continuous source of inspiration. My excellent high-school classmates who happened to also be my university mates in Japan, I didn’t know loneliness because of the supports and good time spent with you guys! Thanks to Xiaoxing Zhou, Xue Bai and Ayumi Takeda for being one of a kind as well as Shuo Zhang, Qingwei Sun, Mengnan An, Chen Wang, Yoko Minamide and so many others for lasting friendship. A lot of thanks to the Better Home Association and the JASSO Honors Scholarship for providing the financial support during my undergraduate and graduate studies in Kyoto University.

Many thanks to my Chinese, Swedish, Canadian, Italian, Dutch and German friends and other friends for nice times spent eating, playing, chatting, and for the peer-pressure of good cooking. Special thanks to Aron Opheij and his warm family, the lovely fairytale-like Laneryd family, Xia Yang, Shuanglin Hu, Xin Hu and Jing Ni, Chongyang Sun and Jon Åslund, Fang Mao and Tao Cui, Wei Xia and Miao Wu, Lois Tang and Luce and Stefano Rubino, Ralph Scheicher, Zhao Qian, Zhigang Wu, Jiefang Zhu, Shi Cheng, Yanling Cai and Di Wu, Yuan Tian, Jia Liu, Bing Cai, Bing Sun, Taha Ahmed, He Xin, Jing Cen and many many others.

Thanks to my family; without your support none of this would have been possible for me.

Thanks to the Swedish Research Council for financially supporting my Ph.D project and Anna Maria Lundin’s scholarship for financing my conference travels and summer school.


[125] Inorganic crystal structure database. http://icsd.fiz-karlsruhe.de/


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology.