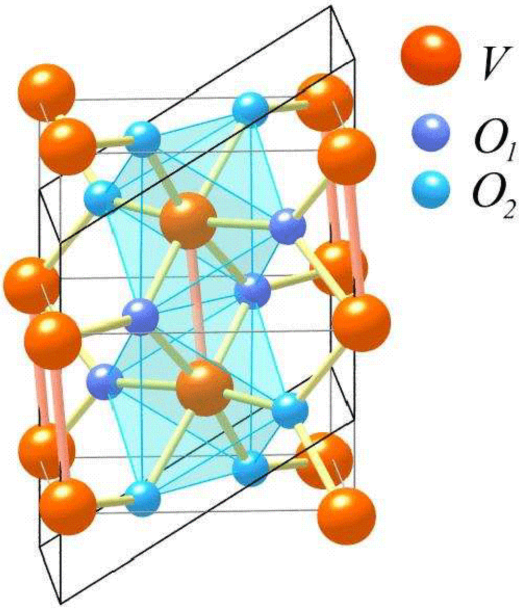
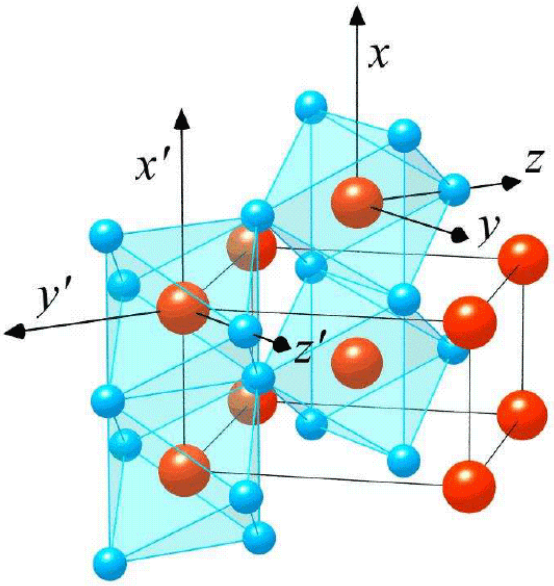
Sol-gel synthesis of VO_2 thin films and the effects of W and Re doping

Claire Moffatt, Anders Wigstein





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Technical report

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Author/s (editor/s)
Claire Moffatt
Anders Wigstein

Project manager
Hans Kariis

Approved by
Sören Svensson

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Scientifically and technically responsible
Stefan Björkert and Eva Hedborg Karlsson

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Sol-gel synthesis of VO2 thin films and the effects of W and Re doping

Abstract (not more than 200 words)

Vanadium dioxide (VO_2) is a thermochromic material that undergoes a semiconductor-to- metal phase transition around 68 °C. This transition is accompanied by changes in the electrical, optical and magnetic properties of VO_2. At room temperature the material is transparent and non-conductive but above the transition temperature the material becomes metallic and IR reflecting. Potential practical applications for VO_2 thin films are, for example, optical (IR) or electrical switching devices and energy-efficient windows. VO_2 has also become interesting in defence applications due to its property to reflect IR radiation. However, for these purposes the transition temperature needs to be lowered which can be achieved by doping of the VO_2 film with other metal cations. In this project the first step was to develop a process for the production of VO_2 films from a vanadium alkoxide precursor by the sol-gel technique. When this was accomplished, doping of the VO_2 films with tungsten and rhenium was performed with doping levels of 1 to 12 at-%.

The crystal structure and the optical switching characteristics were investigated with X-ray powder diffraction (XRPD) and Fourier transform infrared spectroscopy (FTIR), respectively. The surface morphology and chemical compositions of the films were analysed by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). A maximum lowering of the transition temperature was obtained for VO_2 films doped with 4-at% W, resulting in a transition temperature of 22 °C. The Re doping did not succed, no Re could be detected in the films.

Keywords
VO_2 films, spin-coating, sol-gel, vanadium, tungsten doping, rhenium doping

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Författare/redaktör
Claire Moffatt
Anders Wigstein

Projektledare
Hans Kariis

Godkänd av
Sören Svensson

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Rapportens titel (i översättning)

Sol-gel syntes av VO_2 filmer och efekten av W och Re doping

Sammanfattning (högst 200 ord)

Vanadin-dioxid är ett termokromt material som genomgår en fasomvandling från halvledande till metallisk vid en temperatur omkring 68 °C. Denna fasomvandling åtföljs av förändringar i de elektriska, optiska och magnetiska egenskaperna hos VO_2. Vid rumstemperatur är materialet genomskinligt och icke-ledande men över omslagstemperaturen (68 °C) blir det metalliskt och IR-reflekterande. Praktiska tillämpningar för VO_2 tunna filmer är, till exempel, optiska (IR) eller elektriska strömbrytare och energieffektiva fönster. För försvarstillämpningar har VO_2 blivit allt mer intressant på grund av dess egenskap att kunna reflektera IR strålning. För dessa ändamål är det dock nödvändigt att sänka omslagstemperaturen, vilket man kan åstadkomma genom att dopa VO_2 filmen med andra katjoner. Det första steget i detta projekt var att framställa VO_2-filmer med sol-gel teknik med en vanadin-alkoxid som startmaterial. Då detta var utfört dopades VO_2-filmen med wolfram eller renium i mängder mellan 1 till 12 atom %.

Kristallstrukturen och de optiska egenskaperna av VO_2-filmerna undersöktes med röntgen pulver diffraktometer (XRPD) respektive Fouriertransforminfrarödspektroskopi (FTIR). Vidare analyserades filmernas ytmorfologi samt sammansättningen i ytorna med hjälp av svep-elektronmikroskopi (SEM) och röntgenfotoelektronspektroskopi (XPS). Som mest kunde omslagstemperaturen sänkas till 22 °C och det var för filmer dopade med 4 atom% W. Dopaningsförsöken med Re misslyckades, inget Re kunde påvisas i filmerna.

Nyckelord
VO_2-filmer, spin-coating, sol-gel, vanadium, wolframdopning, reniumdopning

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1 Introduction

1.1 Background

Vanadium dioxide (VO_2) is a thermochromic material that undergoes a reversible semiconductor-to-metal phase transition around 68 °C. The phase transition is accompanied by changes in the electrical, optical and magnetic properties of the material [1,2]. Even though VO_2 has been studied extensively for more than forty years, it is still not known in detail how the transition occurs. It is known though, that the transition is due to a structural phase transformation from a low temperature monoclinic structure to a tetragonal rutile structure at high temperature [2,3]. The monoclinic structure is non-metallic and IR-transparent at room temperature but above the transition temperature (68 °C) the material becomes metallic and IR reflecting [4]. For the structures, see Figure 1.

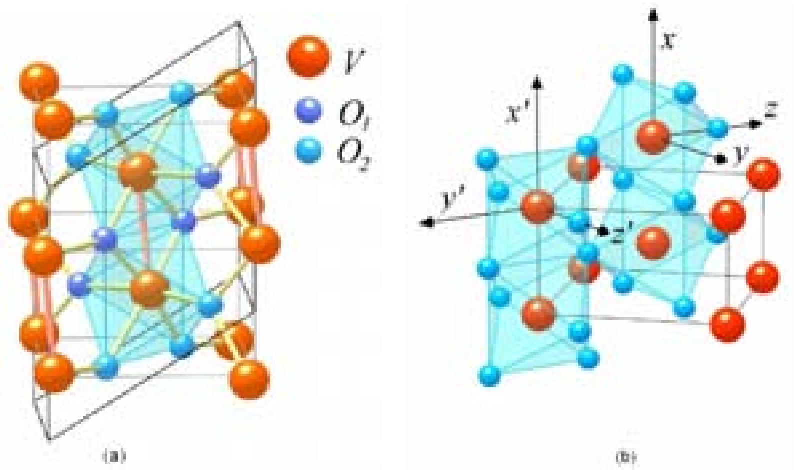

Fig.1 *Crystal structures of (a) monoclinic VO_2 and (b) tetragonal rutile VO_2 [3].*

In the monoclinic structure, vanadium pairing occurs at alternating shorter (2.65 Å) and longer (3.12 Å) V-V bond distances which leads to a doubling of the *c* parameter and opens a gap at the Fermi level[1], making it impossible for the electrons to get into the conducting band hence making the material non-conductive.

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[1] The Fermi level is the level where the most energetic electrons are positioned at 0 K.

In the tetragonal structure, the band gap no longer exists and the electrons can get into the vanadium 3d conducting band, see Figure 2. Thus, the material becomes conducting [1].

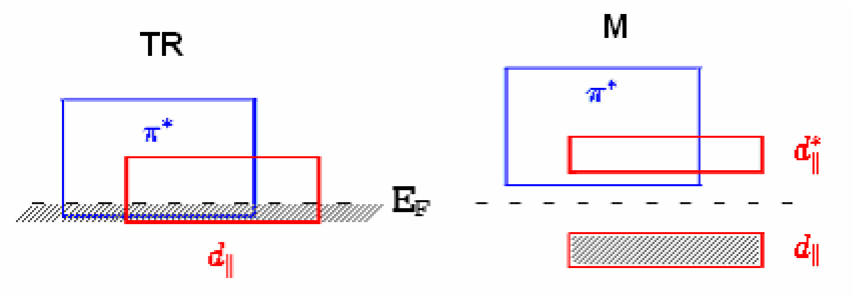


Fig.2 *Schematic band diagrams for tetragonal rutile (TR) and monoclinic (M)* VO_2 *[3].*

Today there are several methods for depositing VO_2 films onto different substrates, for example, reactive magnetron sputtering, chemical vapour deposition (CVD) techniques, dip-coating, spray processes, pulsed laser deposition and spin-coating [5,6,7,8]. Spin-coating provides an easy and inexpensive way to produce thin films and the unevenness in spin coated films is reported to be no more than 1% [9]. These are the main reasons why this technique has been used in this project.

Potential practical applications for VO_2 thin films are, for example, optical (IR) or electrical switching devices and energy-efficient windows [10]. Another application for VO_2 might be for military purposes. Within the Swedish defence, research concerning materials for signature management has been in progress since the 1950s. The reason for this research is to enable troops to work effectively in different environments without the risk of being discovered by enemy sensors. As a result of the technical advances in sensor technology, it is now required that troops and military vehicles *etc.* are able to avoid detection by radars as well as visual detection. It has also become increasingly important to reduce the thermal emissivity, as infrared (IR) sensors are widely used in modern warfare. When it comes to thermal emissivity, signature management mainly concerns the atmospheric transmission windows at 3 to 5 µm and 8 to12 µm. These transmission windows are normally called shortwave and longwave within the IR-region. If a surface has a low emissivity it means that the heat emitted from that surface is lower than the black body radiation and its IR-reflectance is high.

If the emissivity is low, a surface will reflect the surrounding radiation. It follows then that if the emissivity of a surface could be lowered until the apparent temperature of the surface equals the surrounding temperature, it would be possible to elude IR sensors. Hence, if a military vehicle could be coated with a thin film having the capacity to reduce the thermal emissivity sufficiently, it would make it possible to avoid detection by enemy IR sensors. Since the background changes as a vehicle moves through different environments, the signature management needs to be dynamic and controllable. An ultimate objective would be to have a film that could self-adjust its IR-reflectivity depending on what temperature the surrounding is [11]. Another possibility is that the platform (*i.e.* the vehicle) changes its temperature due to *e.g.* sunshine or that the vehicle is driven. In this case one would like to have an adaptive coating to reduce the thermal emissivity. For this purpose it is of interest to use doped VO_2.

The transition temperature can be modified (generally lowered) by doping the VO_2 with other metal cations e.g. tungsten (W), molybdenum (Mo), gold (Au), aluminium (Al), copper (Cu) iron (Fe) *etc.* It has been observed that ions with lower charges, such as Cu^{2+}, Fe^{3+} and Al^{3+}, increase the transition temperature whereas those with higher charges, such as W^{6+} and Mo^{4+}decrease the transition temperature. Doping has also been done with the fluorine anion and that resulted in a decrease in the transition temperature [12].

1.1.1 Doping Theories

Three different theories are presented under this section about what might happen when VO_2 is doped with different cations. They each try to explain which bonds are formed in the VO_2 lattice.

Lu *et al.* [5] did some experiments in 1995 on Cu^{2+} doped VO_2 films and suggested that; When Cu^{2+} ions are incorporated into the VO_2 lattice the monoclinic structure and the tetragonal rutile structure of VO_2 are distorted. This is because Cu^{2+} has different valence and ion radius than the vanadium cations. A result of Cu^{2+} incorporation is that V-O and V-V distances of the VO_2 structures are changed. The valence of vanadium in thin films is still 4+ after the phase transition. The phase transition does not change the surface stoichiometry of the thin film [5].

In 1998, Burkhardt *et al.* [7] studied the effects on VO_2 films doped with tungsten and fluorine and suggested that each tungsten ion breaks up a V^{4+}-V^{4+} homopolar bond. For charge compensation, two W 3d electrons are transferred to a nearest neighbour vanadium ion, thus forming a V^{3+}-W^{6+} and a V^{3+}-V^{4+} pair. The loss of homopolar V^{4+}-V^{4+} bonding destabilizes the semi conducting phase and lowers the metal-semiconductor transition temperature [7].

Manning and Parkin [13] made tungsten doped vanadium dioxide films by the atmospheric pressure chemical deposition (APCVD) reaction of $VOCl_3$, H_2O and WCl_6 in 2004 and suggested that the following process took place:
Tungsten does not form a separate phase but a solid solution with the VO_2. XPS analysis indicated that the vanadium was present in two forms, V^{4+} and V^{3+}, and that tungsten was present as W^{4+}. It was also suggested that the V^{3+} is responsible for the lowering of the metal to semi conductor transition temperature. This means that the V^{4+}-V^{4+} bonds where disrupted in the VO_2(M) by incorporation with W^{4+} and the formation of V^{3+} [13].

1.2 Objectives

The aims of this project were (i) to develop a reproducible process for the synthesis of high quality VO_2 films of by the sol-gel technique and (ii) to try to modify the transition temperature of the film by adding different dopants. Different properties of the doping-ions were looked at to see if that would have an impact on the transition temperature. The dopants tested in this project were Re^{5+}, Re^{7+} and W^{6+} making it possible to compare the impact of ionic species of both charges and sizes. Another aim was to find out whether different co-ions would make a difference or not so for W^{6+} WCl_6 and WO_3 were tested as dopants. The reason for choosing tungsten as a dopant was that it could be used as a reference since a lot of work on tungsten-doped VO_2 films has been done. Rhenium, on the other hand, has not been studied extensively. In the periodic table Re and W are located next to each other in the third row d-elements so it would be expected that they might have similar properties as dopants. Rhenium is also of interest because of its ability to form 7-valent cations. According to previous studies, the transition temperature is lowered more effectively the higher the valence of the cations, so one would expect Re^{7+} to lower the transition temperature more than Re^{5+} and W^{6+}.

1.3 Characterisation methods

Several techniques were used to analyse the samples and are described in sections 1.3.1 through 1.3.4.

1.3.1 FTIR-Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is an important method for observing an entire infrared spectrum. FTIR can be used for identifying organic molecules and is especially powerful when it comes to identifying functional groups in molecules.
In this project FTIR was used to determine the transmittance of the VO_2 films at different temperatures at the specific wavelengths 4 µm (2500 cm^{-1}) and 10 µm (1000 cm^{-1}). When light falls onto a surface it can either be absorbed (***A***), reflected (***R***) or transmitted (***T***). The sum of these three parameters is equal to the incident light I_0. If there is no absorbance the transmittance is the fraction of infrared radiation that passes through a sample and it can be expressed by equation (1).

$$\boldsymbol{T} = I / I_0 \qquad (1)$$

where I = the intensity of the light that has passed through the sample and I_0 = the intensity of the incoming light. If $I \ll I_0$ *i.e.* almost no light will pass through the sample and the $\boldsymbol{T}$ will become low and the reflectance of the sample will be high (if there is no absorbance) [14]. High reflectance indicates a more metallic behaviour. Figure 3 shows an IR spectrum for a VO_2 film at 40 °C.

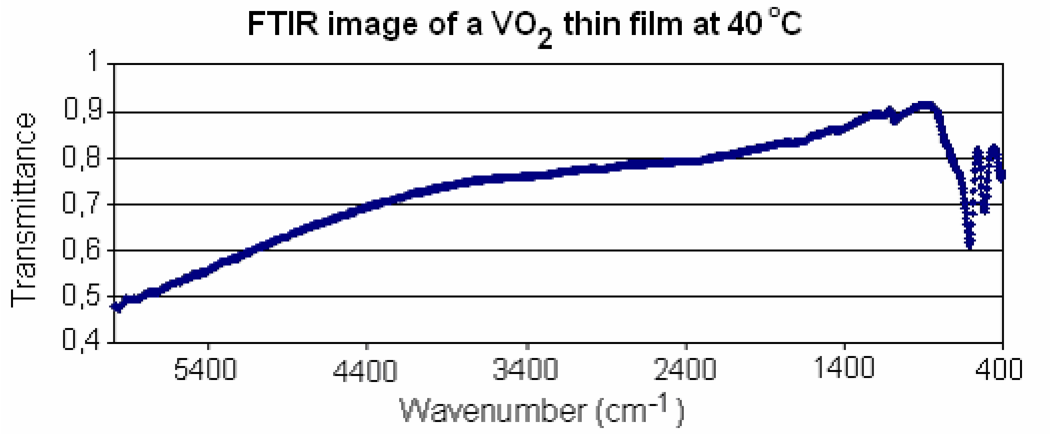


Fig.3 *Transmittance as a function of wave number (cm^{-1}) at 40 °C.*

By changing the temperature of the VO_2 sample, the transmittance also changes due to the properties of VO_2. Thus FTIR can be seen as a tool to measure the transmittance of the VO_2 film at different temperatures. The FTIR spectrum is usually presented as a plot of the transmittance *vs* wave number (400-6000). In this project it was of interest to study the transmittance as a function of temperature for a specific wavelength. The wave numbers 1000 and 2500 cm^{-1} correspond to wavelengths 10 and 4µm, respectively. These wavelengths are in the middle of the atmospheric transmission windows 3 to 5µm and 8 to12µm and hence are of interest in this project. All transmittance *vs* temperature data collected in this project were only plotted for 4 µm because there was not time to do it for both of the wavelengths. However, to evaluate the effect of doping on the transformation temperature, which was the aim of the project, it was not essential to collect the data for 10 µm wavelength. It was possible to heat/cool the samples by means of a temperature chamber, see Figure 4. The temperature was adjusted with a Qterm-J10 Interface Terminal. When the samples were to be cooled the temperature chamber was connected to cooling water. Because the coils in the temperature chamber were very thin, the flow of the cooling water was low and the samples could only be cooled to 25 °C, therefore an extra ice bath was connected to the system which enabled a temperature of 13 °C to be reached.

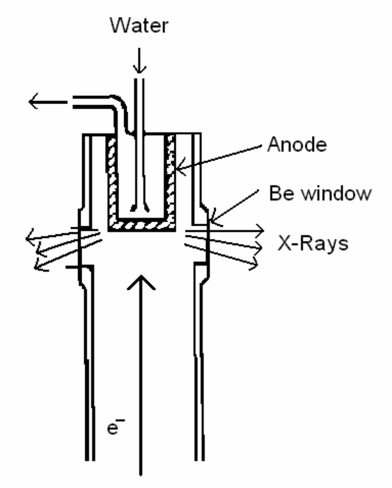
When the temperature was changed it took about 2 to 5 minutes for the temperature to stabilise.

Fig.4 *The temperature chamber that was used in the FTIR. The sample was placed in the sample holder to the left in this picture.*

1.3.2 X-Ray Diffraction

The structures of crystalline solids are most commonly determined by X-Ray diffraction (XRD). With this technique it is possible to determine the precise atomic positions, and bond lengths and angles within a single crystal. With powder diffraction (XRPD) it is only possible

to establish the distance between the lattice planes. A limitation of the XRD technique is that it cannot (usually) identify localized defects or small quantities of dopants.
The X-rays are generated when an electrically heated filament, usually tungsten emits electrons which are accelerated by a high potential difference (20 to 50 kV) and then are allowed to hit a metal target, the anode which is cooled with water, see Figure 5. The anode emits a continuous spectrum of X-rays called "white" radiation. On these white X-rays sharp and intense X-ray peaks (K_α and K_β) are superimposed, see Figure 6.



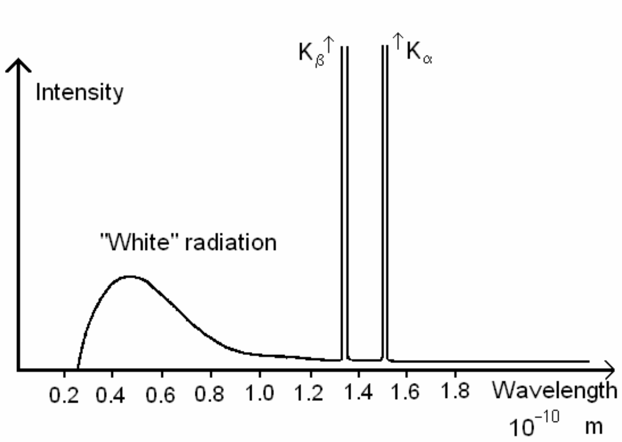


Fig.5 *Section through an X-ray tube [15].*

Fig.6 *An X-ray diffraction emission spectrum [15].*

The wavelengths of the K_α and K_β lines are unique for every anode metal. In X-ray diffraction it is most common to use anodes made out of copper or molybdenum. The lines occur because the energy of the bombarding electrons knocks out electrons from the innermost K shell. This creates vacancies in the K shell which are filled by electrons descending from the shells above. The decrease in energy appears as radiation. The K_α lines occur when electrons from the L shell ($n = 2$) descend and the K_β lines for electrons from the M shell ($n = 3$).
In X-ray diffraction monochromatic radiation is required so one of these lines has to be filtered out and this is accomplished by using an absorbing film and normally the K_β line is filtered out.

In 1913 W.H and W.L Bragg found that crystalline substances gave characteristic patterns of scattered X-radiation. They observed that crystalline materials gave intense peaks of scattered radiation for certain defined wavelengths and incident directions. These peaks are known as Bragg peaks. A crystal was regarded as being made up of parallel planes spaced a distance d apart. To obtain a sharp peak in the intensity of the scattered radiation there are two conditions that must be fulfilled: (1) the incidence angle of the X-rays had to be equal to the angle of reflection and (2) the reflected rays from successive planes had to interfere constructively, *i.e.* that the waves add in phase, producing a larger peak than any wave alone. For the rays to interfere constructively, the path difference (see Figure 7) must be an integer number of wavelengths. This leads to the **Bragg equation,** see equation (2).

$$n\lambda = 2d \sin \theta \qquad (2)$$

The Bragg equation relates the spacing between the planes to the particular angle at which the beams reflect from the planes. In Figure 7, a Bragg reflection from a particular lattice plane is shown. The planes are separated a distance d apart.

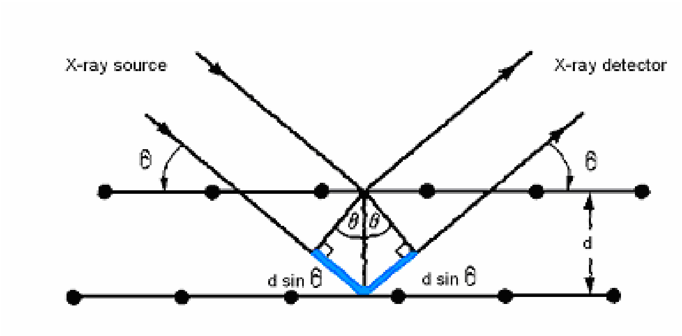


Fig.7 *A Bragg reflection from lattice planes separated by the distance d. The difference in path (marked in blue) for the two incident beams is 2d sin θ, where θ is the incident angle [16].*

In an XRD spectrum the intensities of the diffracted peaks are plotted *vs* 2θ and, as mentioned earlier each compound has its own characteristic peak pattern. In Figure 8, the setup for the X-ray diffractometer is shown and why the diffracted peaks are plotted against 2θ is explained. In this project, the obtained powder patterns were compared with the known pattern for VO_2 to ensure that a crystalline VO_2 film actually had formed [15,16,17]. It was also possible to see if the film contained any other vanadium oxide phases.

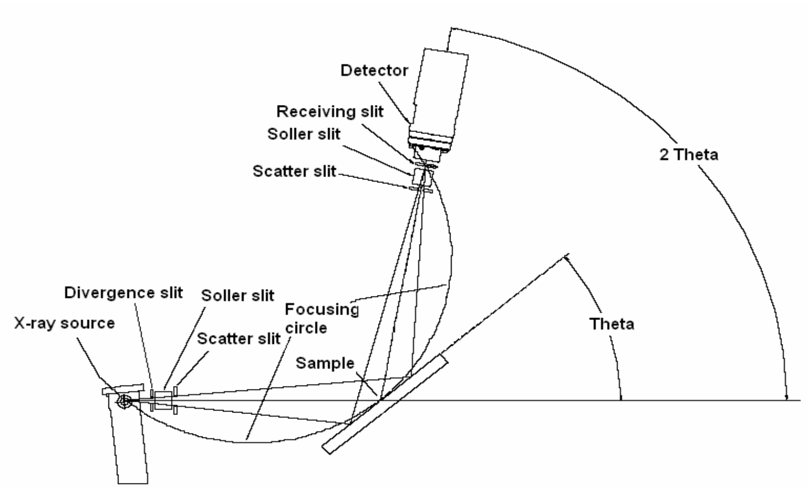


Fig.8 *Setup for the diffractometer giving a sample-to-detector relationship of 1:2 [18].*

1.3.3 Scanning Electron Microscopy

Electron microscopes are instruments that use a beam of highly energetic electrons to examine objects on a very fine scale. The most common type of electron microscope is the scanning electron microscope (SEM). In this technique a high energy (typically 10 keV) electron beam is scanned across the surface of the sample [19]. When the electron beam strikes the sample it causes both electrons and photons to be emitted which for example gives topographical, compositional, and electrical information about the sample, see Figure 9 [20].

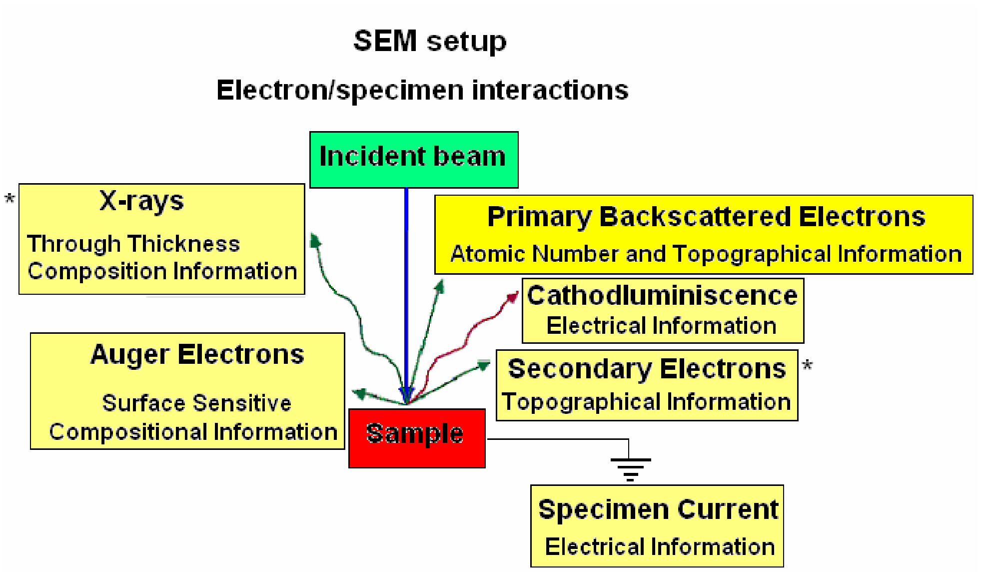


Fig.9 *Schematic picture showing the possible information to get from SEM and EDX [20]. The * indicates the information that was used in this project.*

When secondary electrons are generated some of them escape from the surface and are detected by an electron detector. The out-going signal of the detector is proportional to the number of detected electrons and determines the intensity of the electron beam in the picture tube which then generates a topographic picture of the object [19]. For a schematic picture of a scanning electron microscope see Figure 10.

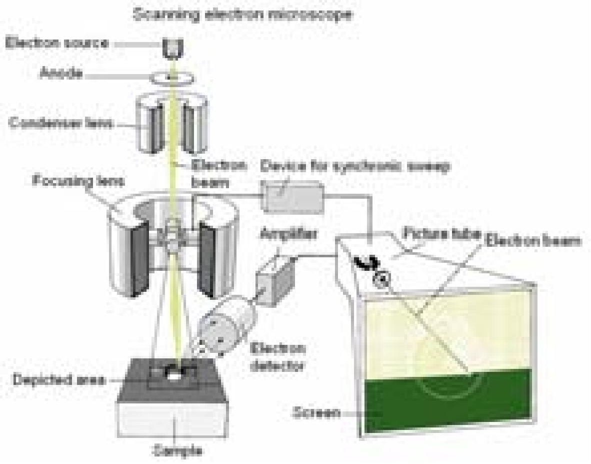


Fig.10 *Schematic picture of a scanning electron microscope [19].*

In conjunction with SEM, a technique called Energy Dispersive X-ray Analysis (EDX) is often used. The incident electrons will cause X-rays to be generated which is the basis of this technique. The energy of the X-rays emitted depends on the material under examination hence information about present elements is obtained [21].

1.3.4 X-Ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a surface sensitive method also known as Electron Spectroscopy for Chemical Analysis (ESCA). The measuring principle is that a sample, placed in high vacuum, is irradiated with well-defined X-ray energy resulting in the emission of photoelectrons. Only those from the outermost surface layers reach the detector. By analysing the kinetic energy of these photoelectrons, their binding energy can be calculated, thus giving their origin in relation to the element and the electron shell.
The energy of the photoelectrons leaving the sample is determined using a concentric hemispherical analyser (CHA) and this gives a spectrum with a series of photoelectron peaks. For a schematic diagram of a CHA see Figure 11. XPS also provides the relative amount of different elements on surfaces with a depth of analysis of only 5 to10 nm (about 10 nm for polymers and papers, lower for metal oxides and metals).

All elements except for very light elements such as H and He can be detected. In addition, information about the chemical environment of the elements, such as the amount of different functional groups, is obtained. Volatile samples cannot be detected with the XPS method due to the ultra high vacuum condition during analysis (pressures below 1 x 10^{-7} torr). In many cases it can also provide information about the valence state(s) of the elements detected [22,23,24].

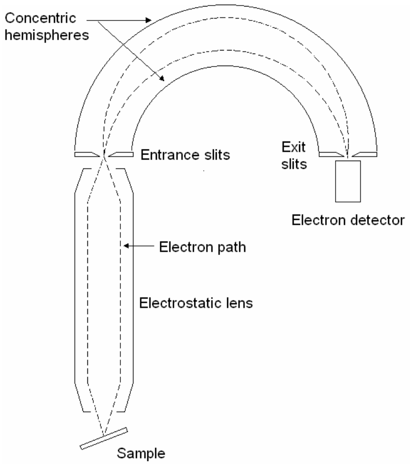


Fig.11 *Schematic diagram of a CHA [23].*

2 Experimental Procedure

The crystal structure of the film was studied by X-ray powder diffraction (XRPD) with a Philips PW 3020 powder diffractometer using Cu K_α radiation. Further settings for the XRPD were:

- 50 mA
- 40 kV
- Nickel-filter
- Divergence slit 1 °
- Antiscatter slit 0.2 °
- Detector slit 1 °

The optical switching characteristics were evaluated as a function of temperature between 25 and 90 °C in a Bruker IFS 55 FTIR-spectrometer with a temperature-controllable chamber. The settings used for the FTIR with the computer software OPUS 5.0 were:

- Resolution = $16 cm^{-1}$
- Source setting = Globar (MIR)
- Beamsplitter = Potassiumbromide (KBr)
- Scanner velocity = 6;10.0 kHz
- Phase resolution = 32
- Apodization function = Blackman-Harris 3-term

Topographic images of the surfaces were recorded by scanning electron microscopy (SEM). The SEM instrument was equipped with an EDX facility providing information about the elemental composition of the samples. The microscope used in this project was a Leo 1550 Gemini with a field emission gun and the detector was a secondary electron detector. For the surface images the acceleration voltage was set to 5 kV and for the X-ray analysis (EDX) the voltage was 20 kV. The chemical composition was also analysed with X-ray photoelectron spectroscopy (XPS). XPS also provided information on the chemical bonding of the elements. XPS spectra were recorded using a Kratos AXIS HS X-ray photoelectron spectrometer. The samples were analysed using a monochromatic Al x-ray source for wide and detail spectra and for the high resolution carbon spectra. The analysis area was about 1 mm^2. In the analysis wide spectra were run to detect elements present in the surface layer.

Detail spectra for each element were followed by quantification to get the relative surface composition. In addition, high resolution carbon spectra were run. These show chemical shifts in the carbon signals due to different functional groups between carbon and oxygen.

2.1 Synthesis of doped and undoped VO_2 thin films

The VO_2 thin film was prepared by mixing vanadium(V)oxytriisopropoxide ($VO(OPr^i)_3$) with isopropanol (Pr^iOH) [33]. The solution was then spin-coated onto a silica (111) substrate. The substrate with the film was then heated in a furnace for 2-2.5 hours between 500-525 °C in a reducing atmosphere (5% H_2 in Ar). This resulted in a transparent and crystalline VO_2 film. Doping of the VO_2 film was done by adding varying concentrations of cations (W^{6+}, Re^{5+} and Re^{7+}) to the sol. Each step in the preparation of the VO_2 thin film is described in sections 2.2 through 2.5. A complete flow diagram over the VO_2 synthesis process can be seen in Appendix 4.

2.2 Cleaning the silica substrate

The Si (111) substrates used as a base for the thin film were 2x2 cm^2. The resistance of the p-doped wafers was 10 to 20 Ω. The wafers were cut out from larger pieces and in that process silica dust was formed. The dust particles adhere to the surface of the silica wafers. To remove the dust and organic substances that may be present on the surface an RCA cleaning procedure was applied, see Appendix 3. After the cleaning procedure the substrates were stored in deionized filtered water until they were to be used.

2.3 Preparation of the vanadium containing sol

The vanadium sol was prepared by mixing vanadium(V)oxytriisopropoxide and isopropanol in the following quantities:

3.5 ml	Vanadium(V)oxytriisopropoxide	($VO(OPr^i)_3$)
26.5 ml	Isopropanol	(Pr^iOH)

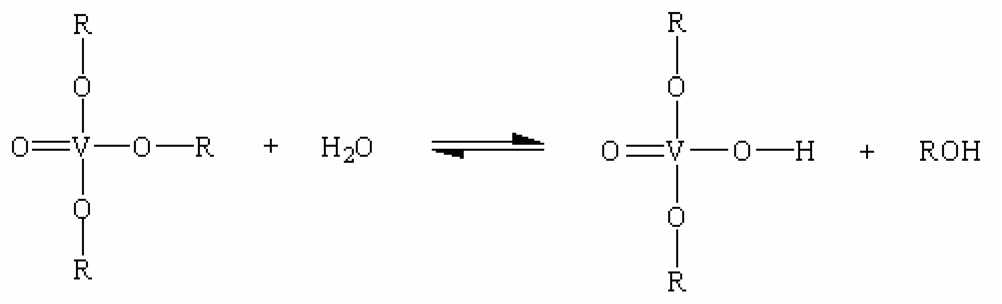
The quantities of the components in the sol had been tested to give the best results regarding reproducibility and quality of the film. The vanadium containing sol is very sensitive to humidity because water starts the hydrolysis and condensation processes in the mixture, see Figure 12. Therefore, the vanadium sol must be prepared in an inert environment. It also implies extra procedures to dry the flasks, needles, syringes etc. to make them completely free from water. The isopropanol used was 99.5 % water free, implying that it had to be treated with molecular sieves to draw out the remaining water.

A more rigorous approach to get the isopropanol water free would be to distillate it and then draw out the remaining water with molecular sieves; however, this did not seem to be necessary in this project.

To get a homogenous mixture, the sol was stirred for at least one hour. After that the vanadium sol was placed in a cool environment for a couple of days to age. The aging process has shown to be of some importance for the surface quality during the spin process. This phenomenon can be related to the fact that some water was still present in the sol which caused the build-up of small vanadium networks due to the hydroxylation and condensation processes.

These small vanadium networks are believed to improve the surface quality when the sol is spin coated. The same positive aging phenomenon has been noticed in other gel systems that stand for a couple of days or even months [25].

Hydroxylation:



Condensation:

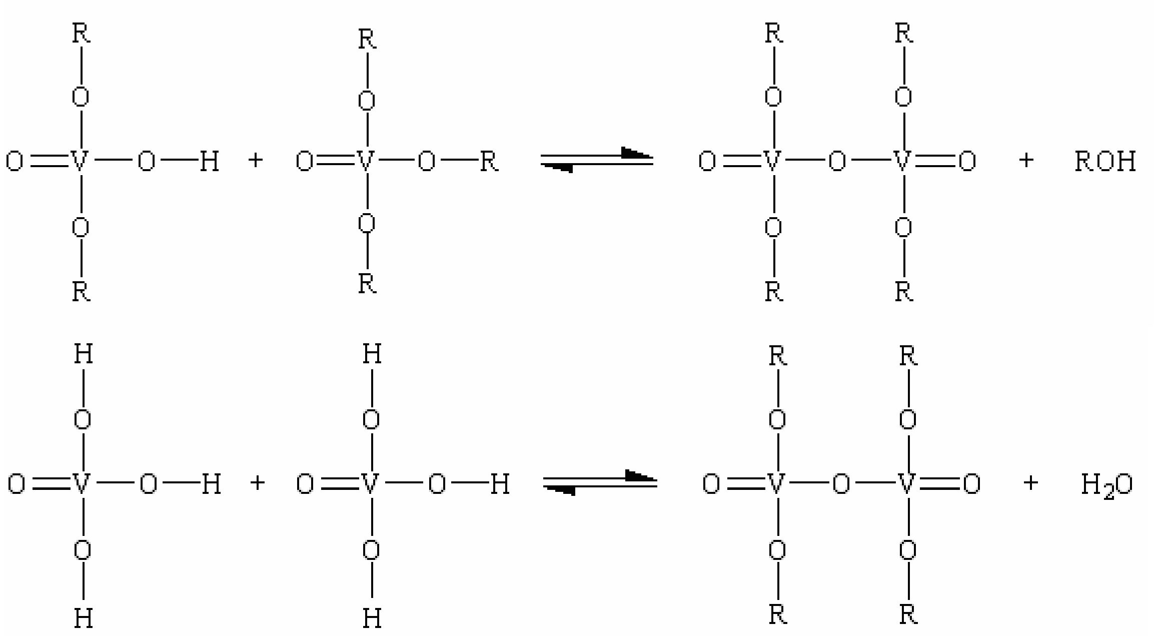


Fig. 12 *When the vanadium sol comes in contact with water the hydroxylation process begins to produce vanadium(V)oxyhydroxodiisopropoxid monomers. These monomers react in either one of two different condensation processes to build up the vanadium oxide network.*

2.3.1 Doping of the vanadium oxide

Doping of the vanadium oxide was made by adding varying concentrations of cations to the sol. The origin of the cations came from the five different compounds listed in Table 1.

Table 1 *Compounds used for doping the vanadium sol.*

Compound	Cation	Molecular formula
Rhenium(V)chloride	Re^{5+}	$ReCl_5$
Rhenium(VI)oxide	Re^{6+}	ReO_3
Rhenium(VII)oxide	Re^{7+}	Re_2O_7
Tungsten(VI)chloride	W^{6+}	WCl_6
Tungsten(VI)oxide	W^{6+}	WO_3

The number of moles of the different dopants added into the vanadium sol was calculated according to equation (3).

$$X_D = \frac{n_D}{n_V + n_D} \quad * \qquad (3)$$

where X_D = the molar fraction in the sol, n_D = the number of moles of the dopant, and n_V = the number of moles of vanadium(V)oxytriisopropoxide. (* For the Re_2O_7 the calculated X_D had to be divided by 2). For further details, see Appendix 1. WO_3, ReO_3 and Re_2O_7 are known to be insoluble in water and only slightly soluble in acids but it was necessary to use isopropanol as solvent since the solubility of the vanadium(V)oxytriisopropoxide had to be taken into consideration [26]. A solution doped with Re_2O_7 was possible to make as long as the concentration corresponding to 2 mol % Re^{7+} in VO_2 was not exceeded. Whenever this concentration was exceeded, the salt did not dissolve completely. However ReO_3 and WO_3 are completely insoluble even in small amounts. As they are soluble in caustic alkalies, an attempt was made to make the solution more basic by bubbling NH_3-gas through it but that did not make any observable difference. Due to lack of time no more attempts to dissolve these oxides were made and, consequently, no other doping than 2 at% with Re_2O_7 was tested.

2.4 Spin coating of a V_2O_5 thin film

Spin coating is used to spread out a more or less viscous liquid onto a substrate with help of the centrifugal force. High rotation speeds are used to evaporate volatile liquids mixed with polymers or solid colloids. This process can be used to produce thin solid films with thicknesses of a few nanometres to a few microns [9].

One of the reasons for not spinning VO_2 directly onto the substrate is that the precursor needed for that, a V^{IV} alkoxide such as $V(OBu^t)_4$, is difficult to synthesize and also highly reactive towards hydrolysis. Furthermore, it is still necessary to heat-treat the vanadium under an inert atmosphere even though the vanadium already has the V^{IV} oxidation state to avoid it being oxidized into V_2O_5. Hence it is more convenient to use V^V oxo-alkoxides as precursors and spin V_2O_5 onto the substrate which then can be easily reduced to VO_2 with heat treatment in a reducing atmosphere [1,27].

The spin coating apparatus used in this project was a Laurell model WS-400-6TFM/LITE. The spinning speed was varied between 2000 and 3000 rpm for 15 to 30 seconds. A spinning speed of 2000 rpm for 30 seconds gave the best results and was later used in all experiments, with the acceleration run at maximum from the beginning until the end.

The spinning was first performed in an inert environment (N_2), but it turned out that spinning in air gave just as good surfaces or even better. The spinning procedure started by first filling a syringe with 1 ml of sol and attaching a filter with a porosity of 0.2 µm and a needle at the end of it. Then the sol was applied onto the substrate and the spinning run was started. When the run was completed the sample was heated, using a halogen lamp, to about 80 °C in order to evaporate the remaining solvent. The spinning process itself evaporates the isopropanol solvent to great extent but some of the solvent is still left. The halogen lamp removes the remaining solvent and drives the condensation reaction to the right creating more V_2O_5.

The colour of the thin film after spinning was mostly yellow with elements of violet and green. Upon drying the film started to turn green. This colour shift is due to the reduction of V^{5+} to V^{4+} in the quantity $V^{IV} / V^V \approx 10\%$ as suggested by Livage and Béteille in [1]. The reduction arises from the remaining organic component, isopropanol [28,29,30]. As V^{5+} is yellow and V^{4+} is blue the green colour implies a mixture of both oxidation states.

Multiple layers of film can be spin-coated onto each other to make the film thicker. Three to five layers of V_2O_5 film with a thickness stretching from 0.07 µm to 0.5 µm have been reported in other projects [1,28]. In this project one or two layers were applied.

2.4.1 Thin film quality problems in the spinning process

A most obvious problem in thin film spinning is to make the substrate completely clean from dust and organic materials. The problem can be reduced by the RCA cleaning procedure described in section 2.2. Other more complicated problems such as cloudiness, orange peel and radial striations can still affect the final result of the film.

A cloudy film is characterized by an opaque appearance. This happens when the solvent and the polymer used are only partially miscible. When the spinning starts, evaporation takes place, increasing the polymer concentration beyond its solubility limit. This causes the polymer to precipitate. This points out the importance of choosing a solvent and a polymer that do not phase-separate. Orange peel and radial striations are less well understood and accurate information about their origin and appearance is not available [9].

2.5 Reduction of the V_2O_5 to crystalline VO_2

Different phases of vanadium oxide can be formed from V_2O_5 during the heating process in a reducing environment (5 % H_2 in Ar). The phases formed are related to, *e.g.* temperature, the flow of the reducing gas, how long the reduction process lasts and whether a preheating step (with the purpose of eliminating organic materials in the film) is used or not.

The heating process used in this project was 525 ºC for 2.5 hours with a constant flow of a reducing gas (5 % H_2 in Ar). This resulted in a crystalline VO_2 phase. At first 500 ºC for 2 hours was used but XRD showed that there was still too much unreduced vanadium phases present at that setting. Therefore 30 minutes was added to the reducing process time so that more VO_2 would be produced. A preheating step in vacuum was also used under the first test samples (not included in this report) but that resulted in bad quality films. These films are characterized by many mixed vanadium phases and have non transparent appearance. The redox reaction taking place in the furnace can be schematically described as follows:

Reduction:

$V_2O_5 + 2e^- \rightarrow 2VO_2 + O^{2-}$

Oxidation:

$H_2 + O^{2-} \rightarrow H_2O + 2e^-$

Reduction-Oxidation:

$V_2O_5 + H_2 \rightarrow 2VO_2 + H_2O$

3 Results and Discussion

The presentation of XRPD, EDX and temperature *vs* transmittance graphs for the most interesting thin films will be presented in sections 3.1 and 3.2. SEM images will be given under their own section. The synthesis conditions for the various VO_2 films (denoted A1-A25) are given in Appendix 2. The transmittance scale in the temperature vs. transmittance graphs goes from 0 till 1, where 1 means 100 % transmittance.

3.1 The reducing process in the furnace

If the flow of reducing gas (5 % H_2 in Ar) was insufficient during the heating a mixture of vanadium oxide phases such as V_6O_{13}-V_2O_5-V_4O_9-VO_2 was obtained. The various vanadium oxide phases could be identified by their X-ray diffraction patterns. One example is shown in Figure 13. If the reduction time was too short the same mixed phases as mentioned above could be seen. When the reduction step was too long the formation of the V_2O_3 phase was seen and thus the vanadium had been over reduced. The peaks for values on 2θ around 12 to 15 might come from partially hydroxylated $VO(OR)_{3-x}(OH)_x$ species. This argument is supported by the fact that low values for 2θ mean that the distance between the lattice planes, d, is larger than for the higher values for 2θ. Since hydrogen bonds are relatively weak bonds, it is reasonable to think that these would increase the distance between the lattice planes. Furthermore, this is also supported by observations made by Livage [4].

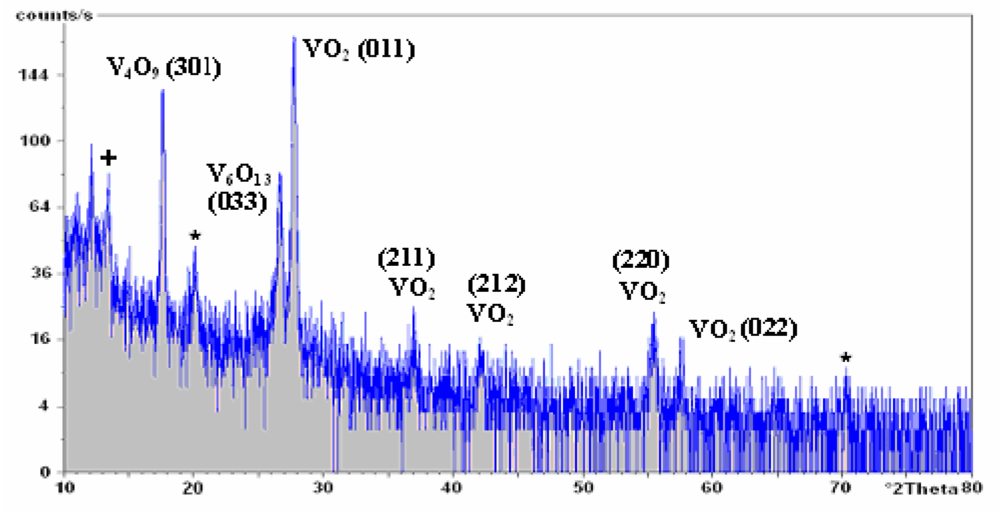


Fig.13 *X-Ray powder diffraction pattern for sample A7 showing mixed phases of vanadium oxide. The strong peak at 2θ=27.8; 3.21Å indicates the dominant VO_2 (011) phase. The * suggests mixed vanadium phases and the + suggests hydrogen bonds between the film layers. The numbers in brackets indicates from what plane the diffraction originates.*

3.2 Transition temperature

3.2.1 Undoped VO_2 film

The transition temperature for sample A1 was $T_T = 68.5$ °C as seen in Figure 14. Sample A1 contains almost pure VO_2, as verified by the XRD graph seen in Figure 15. The transition temperature changes upon heating or cooling the VO_2 film causing a hysteresis loop behaviour. For this VO_2 film $\Delta T_H = 5$ °C for the hysteresis loop. The width of the hysteresis loop is explained by the fact that the VO_2 microcrystals switch independently from the semi-conducting to metallic state. In films with larger crystals a cooperative switching behaviour can be seen, which results in narrower hysteresis loops [30].

The arrows in Figure 12 indicate in which direction the heating/cooling process goes. A very large drop in transmittance, 76 % is seen at the transition temperature.

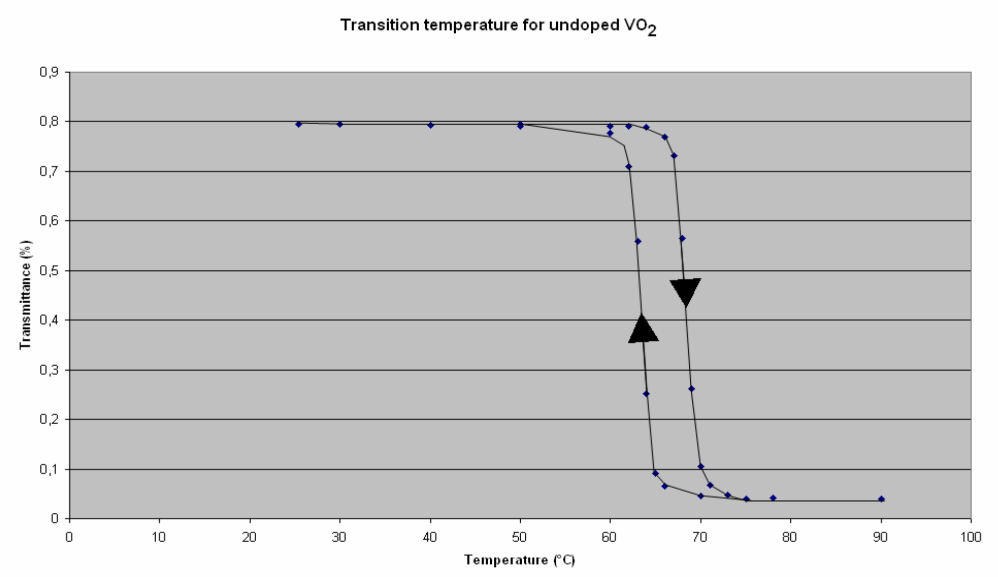


Fig.14 *Transition temperature for an undoped* VO_2 *film. Sample A1.*

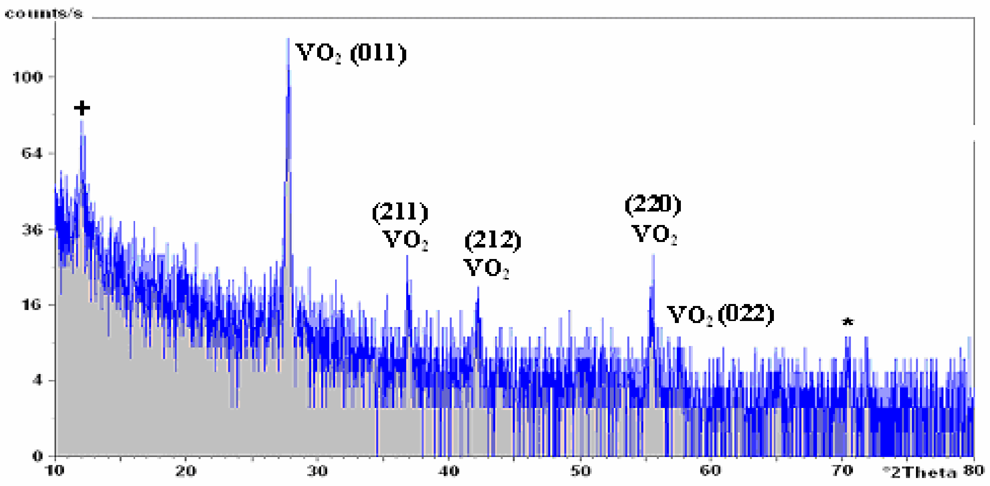


Fig.15 *XRD powder pattern for undoped* VO_2*, sample A1.*

3.2.2 VO_2 film doped with WCl_6

The vanadium sol turned bright yellow upon adding WCl_6. After 30 min of stirring the solution shifted colour from yellow to blue. This is said to occur because W^{6+} (yellow) is reduced to W^{5+} (blue) by the organic solvent, as suggested by Livage and Ganguli [6]. The organic solvent in this case was isopropanol. This leads to the question: is W^{5+} further reduced to W^{4+} or even W^{3+} by the isopropanol? No experiments have been conducted to confirm or refute this. It could be important to know this for the understanding of the incorporation process of tungsten into the VO_2 lattice or more interesting if tungsten is incorporated into the vanadium network in the mixing process of the vanadium sol?

Addition of 1, 2 and 4 at% WCl_6 in VO_2 was tested. Higher doping concentrations of tungsten than 4 at% were not tested because beyond that concentration the optical contrast becomes so weak that the transition is almost not visible as mentioned by Béteille and Livage [1]. The transition temperatures shifted from T_T = 48 °C for the 1 at% doped to T_T = 22 °C for the 4 at% doped samples, see Figures 16-18. The transition temperature for the sample with 4 at% doping, which was lowered to 22 °C is satisfactory, but as can be seen in Figure 18 the transmittance in the semi-conductor state is poor, starting at only 43 %. Compared to undoped VO_2, a much poorer transmittance drop was seen at the transition temperature for the doped VO_2 films with higher quantities than 1 at% WCl_6. The same phenomenon was also seen by Béteille and Livage [1]. Variations in film thickness between the samples have not been taken into consideration when comparing results with each other. The hysteresis loop assumes a wider and more elongated appearance with increased doping.

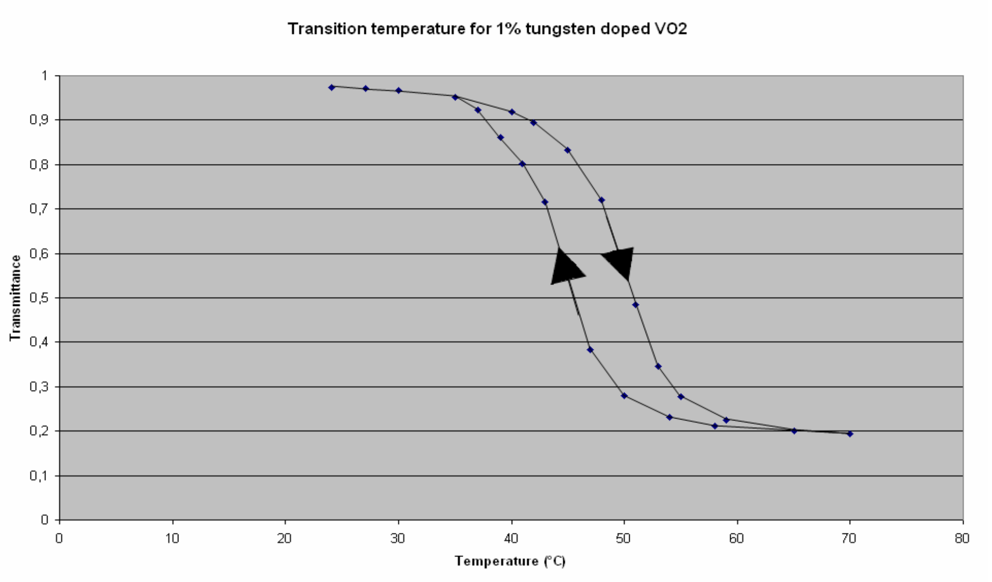


Fig.16 *Transition temperature T_T = 48 °C for a 1 % tungsten doped VO_2 film. Sample A22.*

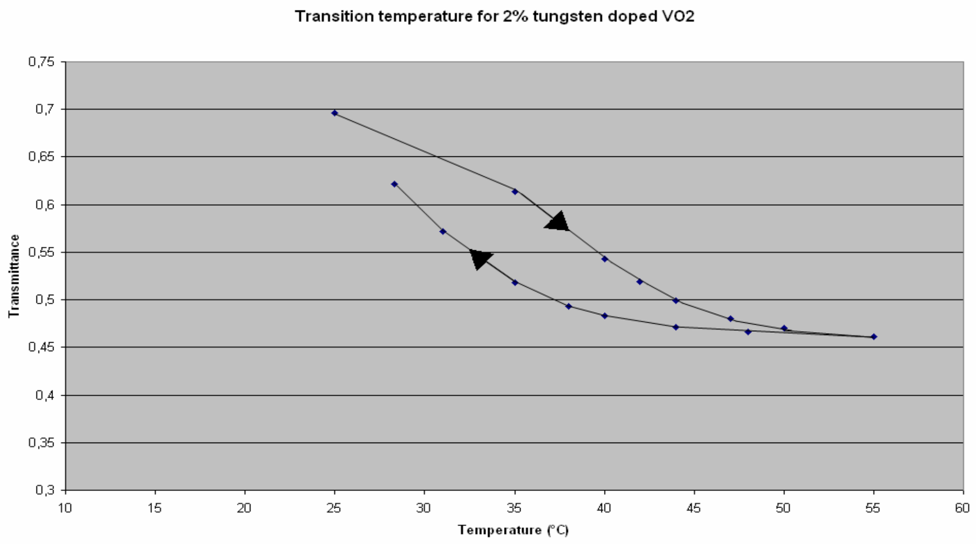


Fig.17 *Transition temperature T_T = 38 °C for a 2 at % tungsten doped VO_2 film. The unfinished graph is due to insufficient cooling devices in the FTIR. Sample A19.*

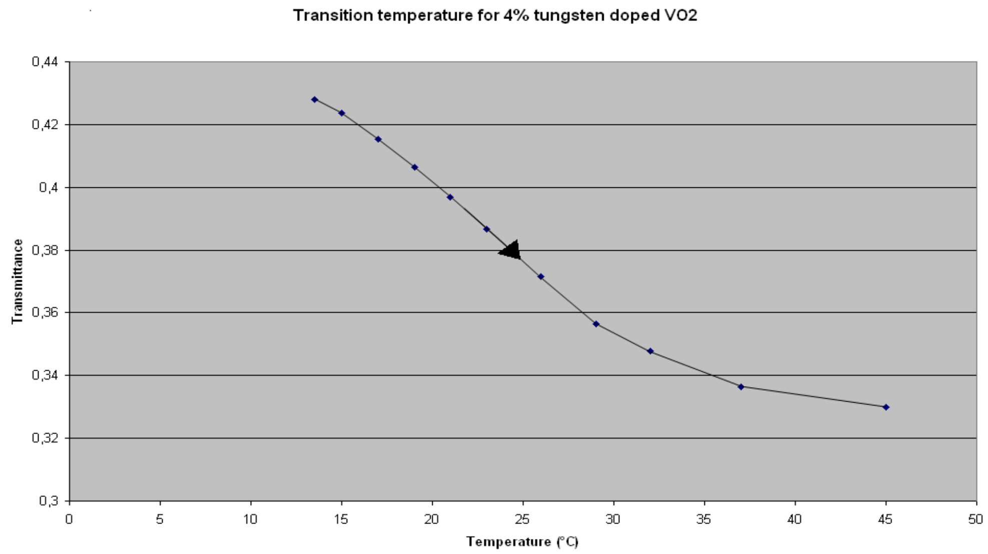


Fig.18 *Transition temperature T_T = 22 °C for a 4 at% tungsten doped VO_2 film. Only heating was preformed on the sample. Sample A23.*

The hysteresis loops for samples A22 and A19 were ΔT_H = 5 °C and ΔT_H = 7.5 °C respectively. The XRPD graph for sample A22 is shown in figure 19. There are strong V_4O_9 and V_6O_{13} peaks indicating that A22 has not been fully reduced. When the films were doped, there were more non-reduced vanadium oxide phases still remaining after the reduction process, so the conclusion drawn from this was that a longer reduction step would be necessary for doped films to receive a more pure VO_2 phase. All samples had a reduction step of 2.5 h except for sample 25 that got a half an hour longer reduction step. Comparing the XRPD graphs for a doped sample with a reduction time of 2.5 h with that of 3 h it can be seen that the longer reduction time yields more reduced vanadium, but it is still not fully reduced. Hence, an even longer reduction step should probably have been used for the doped samples to get a pure VO_2 phase. However, there was not enough time to look into this.

Peaks for tungsten oxide phases were not seen in the XRPD graphs for the tungsten doped samples. This indicated that the dopant had not formed a separate phase but that tungsten was incorporated in the VO_2 lattice [13].

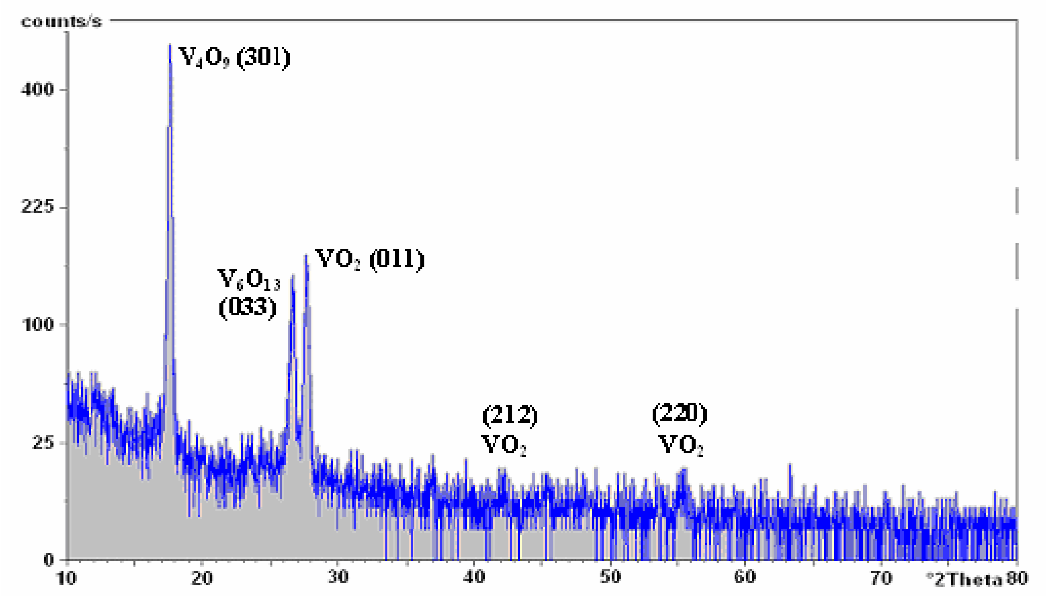


Fig. 19 *XRPD for sample A22 doped with 1 % tungsten. The reduction of the vanadium phases has not gone to completion.*

Note also that no chlorine compounds were detected in the XRD powder pattern for the WCl_6 doped samples or the $ReCl_5$ samples. Observations made with EDX, see Figure 20, confirm that no chlorine was present in the film. This has also been verified by Manning and Parkin [13].

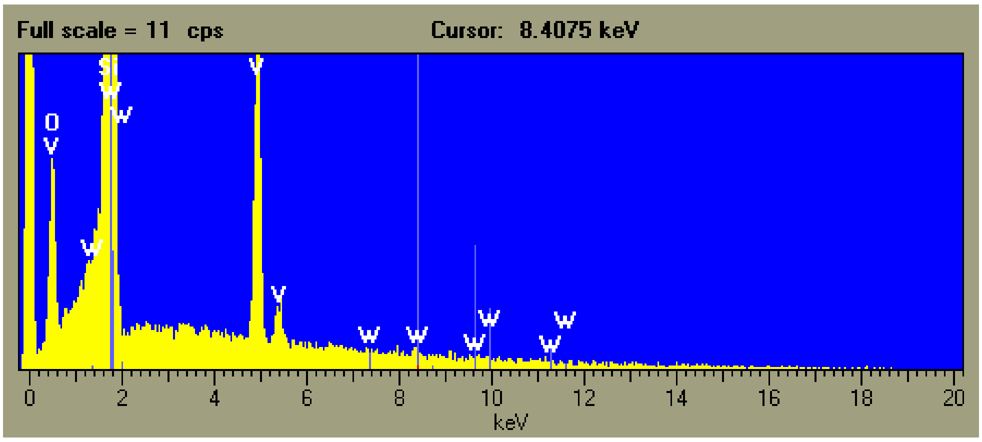


Fig.20 *EDX image showing that no chlorine is present in the VO_2 film and that tungsten is present in the film. Sample 23.*

A theory for the missing chlorine could be that it is evaporated in the heating process either as Cl_2, HCl or in some other form.

3.2.3 VO_2 film doped with $ReCl_5$ and Re_2O_7

When $ReCl_5$ was mixed into the vanadium sol the solution became dark green. To dissolve the added $ReCl_5$, several hours of stirring were required. The solution turned pale yellow when Re_2O_7 was used as a dopant and several hours of stirring were also required in this case to completely dissolve the material. Figure 21 shows the transition temperature for a VO_2 film prepared with 2 % Re_2O_7. As mentioned earlier it was not possible to get a higher percentage than 2 % with Re_2O_7 as it is only partially soluble in acids.

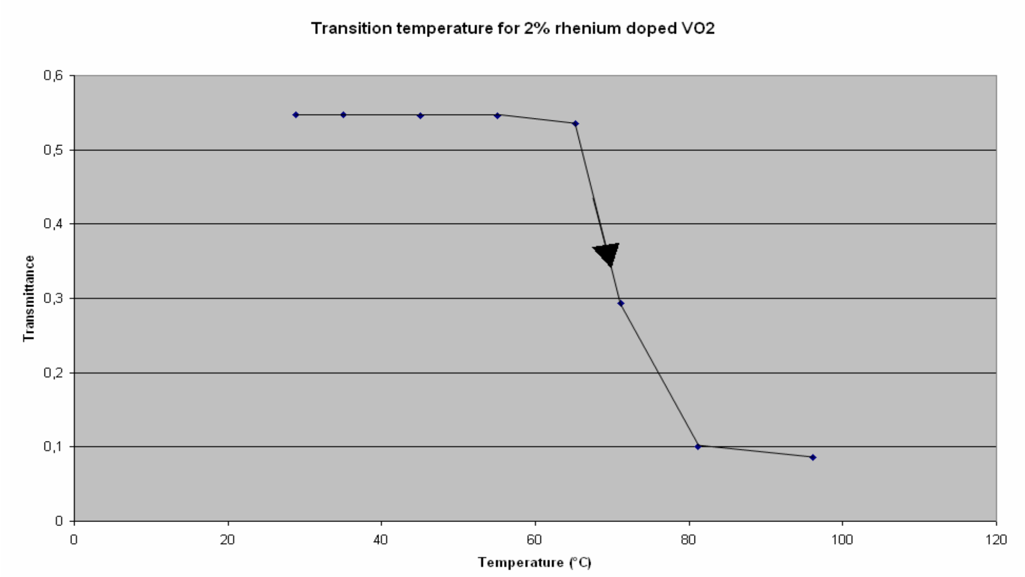


Fig. 21 *Transition temperature for a VO_2 film prepared with 2 % Re_2O_7. This was the first test to see if rhenium could lower the transition temperature. Sample A12.*

A look at Figure 21 reveals that the attempt to dope with rhenium does not lower the transition temperature since T_T = 68 °C. Another experiment was done with 12 % rhenium doping to be absolutely sure that rhenium did not lower the transition temperature even the slightest. The result can be seen in Figure 22. XRPD for the VO_2 film prepared with 12 % rhenium can be seen in Figure 23.

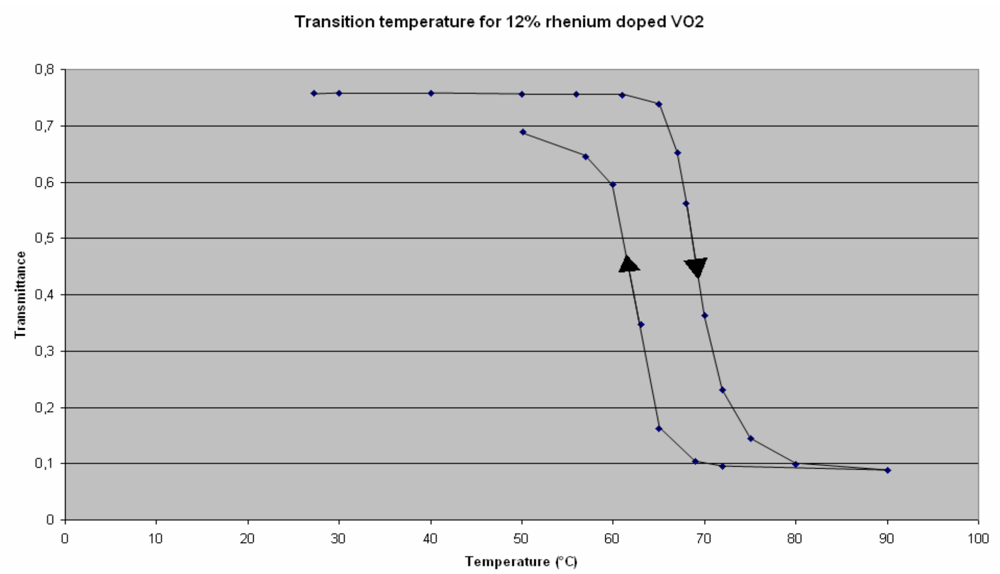


Fig.22 *Transition temperature for VO_2 prepared with 12 % Re. Rhenium does not seem to have lowered the transition temperature to any extent. Sample A25.*

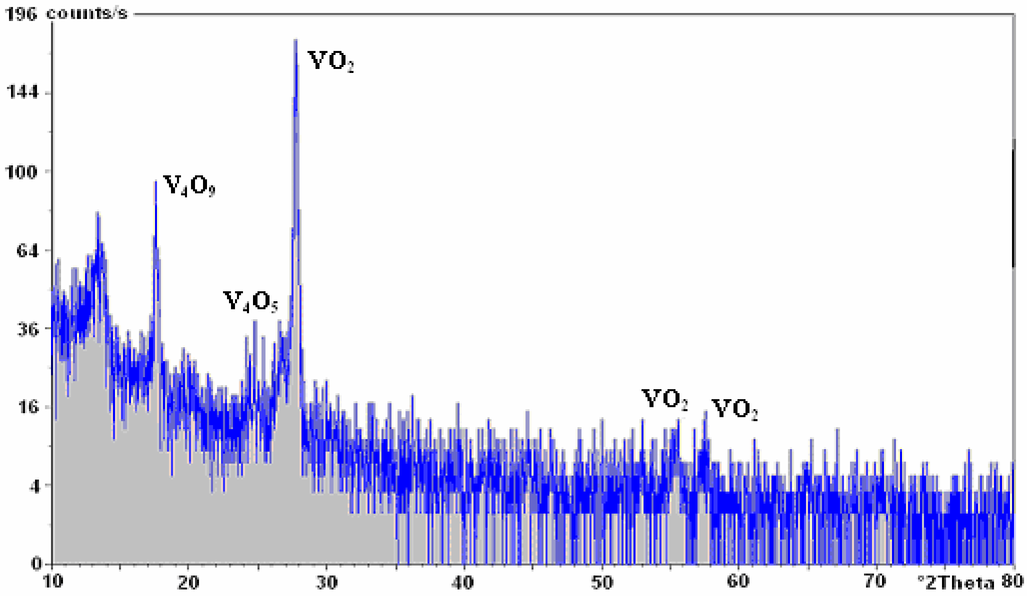


Fig.23 *XRD powder pattern for the VO_2 film prepared with 12 % rhenium. This sample received a 3 hour long reduction step, which resulted in smaller peaks for the unreduced vanadium oxide phases. Sample A25.*

Figure 22 confirms that the attempt with rhenium has not lowered the transition temperature for the VO_2 film.

Sävborg and Nygren made some studies on $V_{1-x}Re_xO_2$ systems. They found that the transition temperature for a rhenium doped VO_2 system could be lowered by 18 K/at % Re when $x \leq 0.07$ [31]. The difference between this project and theirs is the method used for doping and producing the VO_2 film. They used sealed evacuated silica tubes filled with the proper chemicals V_2O_3, V_2O_5 and ReO_2 that were heated to 1275 K for 7 days. This resulted in a few rhenium doped VO_2 crystals that were analysed with XRD and DTA (differential thermal analysis). They also studied the magnetic susceptibility and electrical conductivity of the films. In this project, on the other hand, the sol-gel technique was used and the film was spin coated onto the substrates and reduced in a furnace. Furthermore, the rhenium and tungsten doping attempts was performed at room temperature. This difference in methods for producing and doping the VO_2 film with rhenium might explain the fact that Sävborg and Nygren succeeded where this project failed.

Despite the fact that higher temperature and other methods might be necessary to succeed in incorporating the rhenium into the VO_2 lattice, the question still remains. *Why did it not work to dope the VO_2 with rhenium using the methods in this project?*
EDX analysis of sample A12 (2 at% Re_2O_7) also confirmed that no rhenium was present in the film. A difference that can be noted right away is that tungsten changed colour in the mixing process with the vanadium sol whereas rhenium did not. At first it was suggested that rhenium was harder to reduce than tungsten which might be necessary for the incorporation in the VO_2 lattice (several reports have pointed out that tungsten was present in reduced form in the VO_2 film, see section 1.1.1 for one example). But it turned out that rhenium is easier to reduce than tungsten. Another difference between tungsten and rhenium is their radius. Tungsten has a covalent radius of 146 pm while rhenium has a covalent radius of 159 pm. A theory that rhenium was too big to be incorporated into the VO_2 lattice was suggested. This could not be the case though, because Sävborg and Nygren succeeded in their rhenium doping [31]. See table 2 for information about other VO_2 film dopants, their covalent radius and impact on the transition temperature.

Table 2. *The change in transition temperature is estimated. The estimate is based on relevant reports in the subject. No source will be defined because of result variations.*

Substance	**Covalent radius (pm)**	**Change in transition temperature**
Rhenium	159	- 18.0 °C/1 at%
Tungsten	146	- 23.0 °C/1 at%
Molybdenum	145	- 20.5 °C/1 at%
Gold	144	- 16.5 °C/1 at%
Titanium	136	± 0.0 °C/1 at%
Lithium	134	- 8.0 °C/1 at%
Iron	125	- 6.0 °C/1 at%
Vanadium	125	------------------
Aluminium	118	+ 11.0 °C/1 at%
Phosphors	106	- 2.0 °C/1 at%
Fluorine	71	- 19.0 °C/1 at%

Table 3 shows the XPS results for samples A9, A23 and A25. Sample A23 was doped with 4 at% tungsten but XPS indicates 2.2 at%. This number comes from the fact that N, Si and C also are present in the film. A recount of the tungsten content shows that sample A23 actually contained 3.03 at%. This means that 25% of the tungsten was not incorporated into the VO_2 lattice. What is more noticeable in the XPS results is the rhenium content in sample A25. None of the rhenium from the $ReCl_5$ compound is present in the VO_2 film, even with the high 12 at% doping attempt. This is in line with the EDX results and the transition temperature graphs for the rhenium doped samples.

Table 3. *Relative surface composition (at%).*

Sample	**Atom %**						
	C	**O**	**V**	**Re**	**W**	**N**	**Si**
VO_2 (undoped, A9)	21.6	52.5	20.6	-	-	2.4	2.9
W - VO_2 (4 % W, A23)	24.4	51.1	19.2	-	2.2	1.7	1.5
Re - VO_2 (12 % Re, A25)	22.2	51.8	20.9	-	-	2.8	2.4

- = signal at noise level in detail spectra (below about 0.2-0.5 at %)

Rhenium was present in the vanadium containing sol before spinning but not after the reducing process in the furnace, as confirmed by the XPS and EDX results, therefore experiments where made that confirmed that Re was present after spin coating. This might indicate that the Re dopants upon reduction forms volatile species that are transported away from the film by the gas flow. The volatile species could be the molecules Re_2O_7 and $ReCl_5$ which have boiling points at ~300 °C and ~220 °C respectively. If these molecules are present at the surface of the film after the spin procedure they would disappear in the reduction process since the temperature in the furnace was 525 °C. Another possibility is that volatile carbonyl compounds were formed such as $Re(CO)_x$, the C originating from the solvent. It could also be possible that a mixture of the organic compounds and the Re-species were formed. To confirm this further experiments are needed, however.

XPS analysis of sample A9 shows that vanadium is present in the form V^{5+} and V^{4+}. V_2O_5 has a peak for V 2p at 517.6 eV and VO_2 a peak at 516.3 eV. According to the XPS results a peak at 517 eV was recorded for the V. The quota O/V ≈ 2.5, which indicates that vanadium is present as V_2O_5, but some of the oxygen comes from the carbon signal, hence the actual quota is smaller than 2.5. When O/V comes closer to 2 more VO_2 is present in the film. It is reasonable to think that there is a mixture of both V_2O_5 and VO_2.

It was more difficult to decide the valence of the W in the film because the strongest peak, W 4f, for sample A23 was overlapped by the V 3p peak and thus giving no useful information, see Figure 24. However, the peak at 248 eV implies, according to references, that the W was present in oxidised form. The unoxidised peak lies at 243 eV. The difference between these states is 5 eV.

In the Handbook of X-ray Photoelectron Spectroscopy it is possible to see the different positions of the W 4f peak and they are: 31.4 eV for unoxidised W, 32.8 eV for WO_2 (W^{4+}) and 35.8 eV for WO_3 (W^{6+}). The difference between the unoxidised W and the W^{6+} is 4.4 eV, which is close to the 5 eV that pertain to the W 4d peak. If it is assumed that the shifts upwards in binding energy are the same for 4d as for 4f it is most reasonable to think that the W is present as W^{6+}.

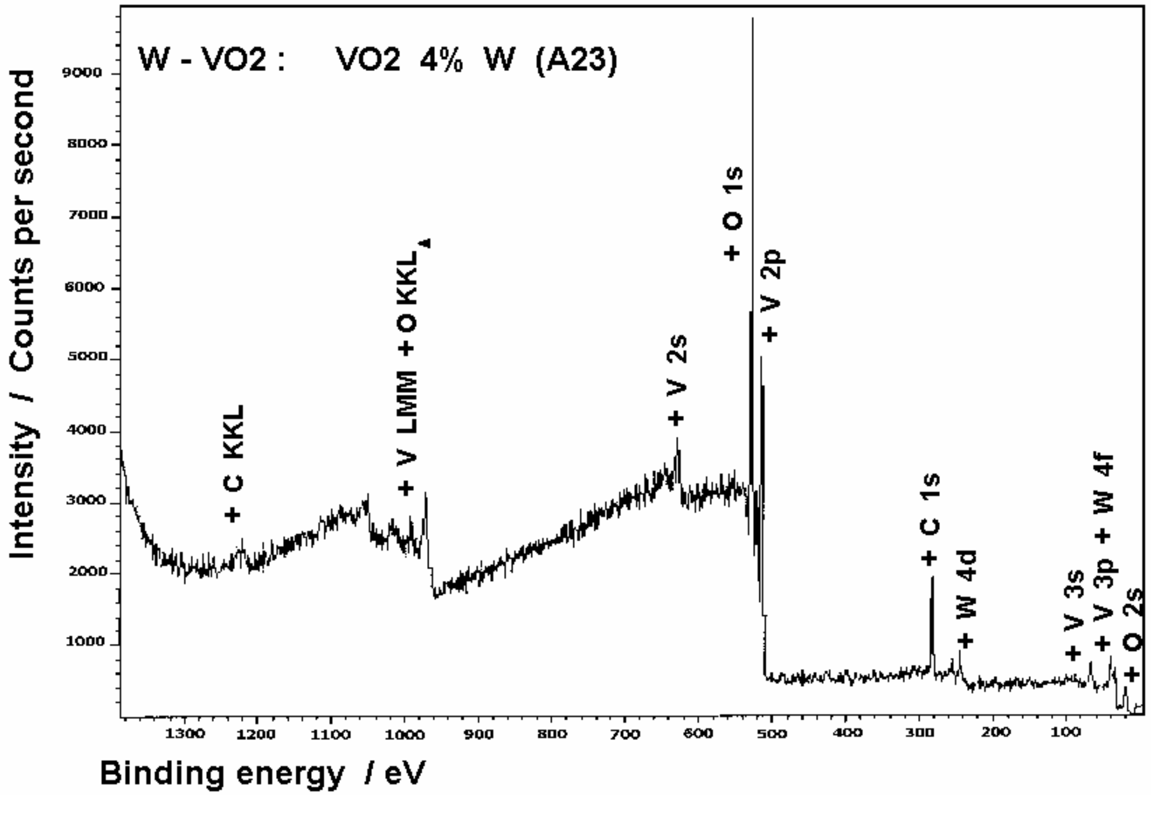


Fig.24 *XPS Detail spectrum over a vanadium film doped with tungsten showing the overlap of the V 3p and W 4f peak.*

3.3 Topography

SEM was used to study the surface topography of the VO_2 films and to measure the film thickness. To estimate the thickness a cross-section sample was prepared. This sample did unfortunately not produce any images that were useful. Instead an image taken earlier on a crack in the film, see Figure 25, was used to make estimation about the film thickness. The edges were estimated to be 1µm thick. Sample 23 was spun with 2 layers; hence each layer was thought to be about 0.5 µm thick. It should be mentioned that it is just a rough estimation.

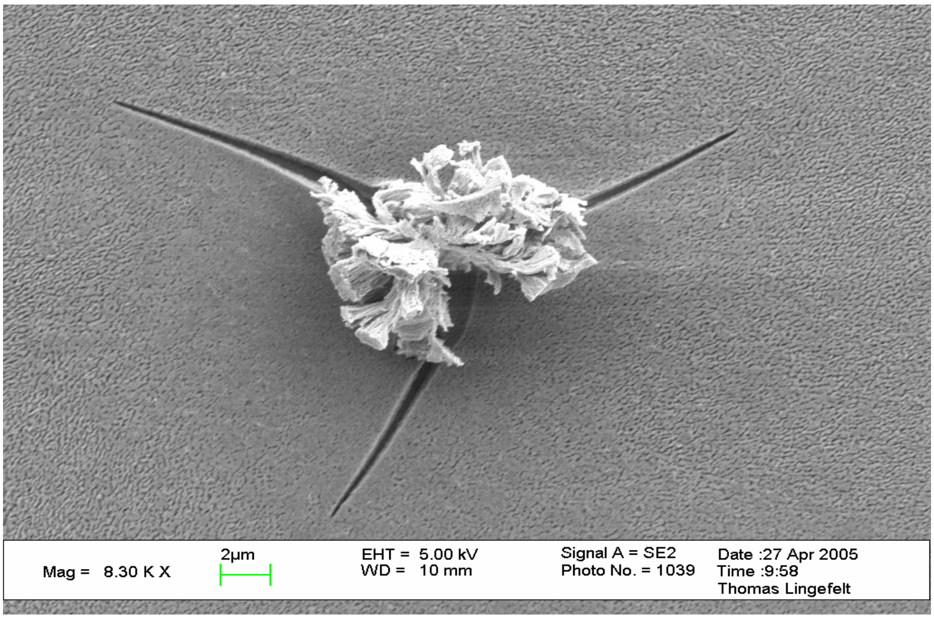


Fig.25 *SEM image on a crack where a paper particle has been trapped. Sample A23.*

Figure 26 shows an image from the edge of the substrate where the film has flaked off. When a film is spin coated the viscosity near the edge is lower than at the centre which results in a thinner film at the edges hence the flake off effect occurs [9]. This phenomenon has been observed in almost every film done in this project.

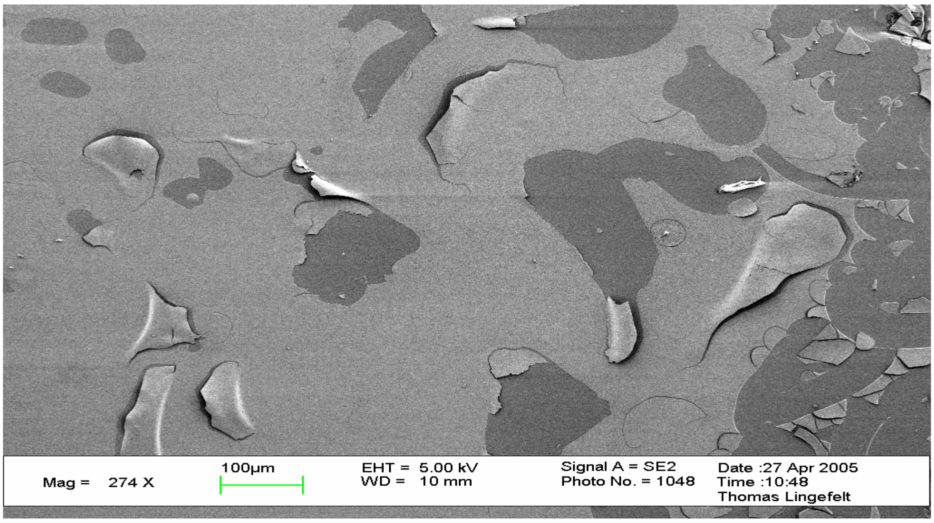


Fig.26 *SEM image showing the edge on sample A12.*

All of the surfaces in Figure 27 have experienced the same heat treatment. As can be seen there are notable differences between the surface structures, for example sample 12 is divided into big islands while sample A8 has a more linked structure. The linked structure is a result of abnormal grain growth of grains with lower interfacial energy due to a special orientation. These grains consume all other grains with an energetic less preferred orientation and the result is a more linked structure. Simultaneous with this grain growth is an instability which causes the film to break up into islands. Thermodynamically, this phenomenon can be explained by the fact that the break up process lowers the free energy of the film and this occurs when the grain size to film thickness ratio exceeds a critical value. The difference in linkage can also be related to difference in interfacial energy due to different chemical composition [32].

Surface energies are very sensitive to impurities. Doping or dirt can act as impurities thus it lowers the surface energies. Sample A8 and sample A9 are both undoped but the texture of their films is not the same. Sample A8 is very contaminated by dirt and other unknown particles, so it has lower surface energy than sample A9. The difference in linkage and smaller amounts of islands in sample A8 can therefore possibly be explained by that. However, the transition temperature and the quality of the film in sample A8 did not seem to be affected by the dirt. An FTIR-analysis showed that the T_T = 68 °C and the transmittance drop was 86 %. The transmittance drop would probably have been bigger if the sample had not been contaminated since the contaminants on the surface scatter the light in the FTIR and thus the transmittance in the semiconducting phase is lowered.

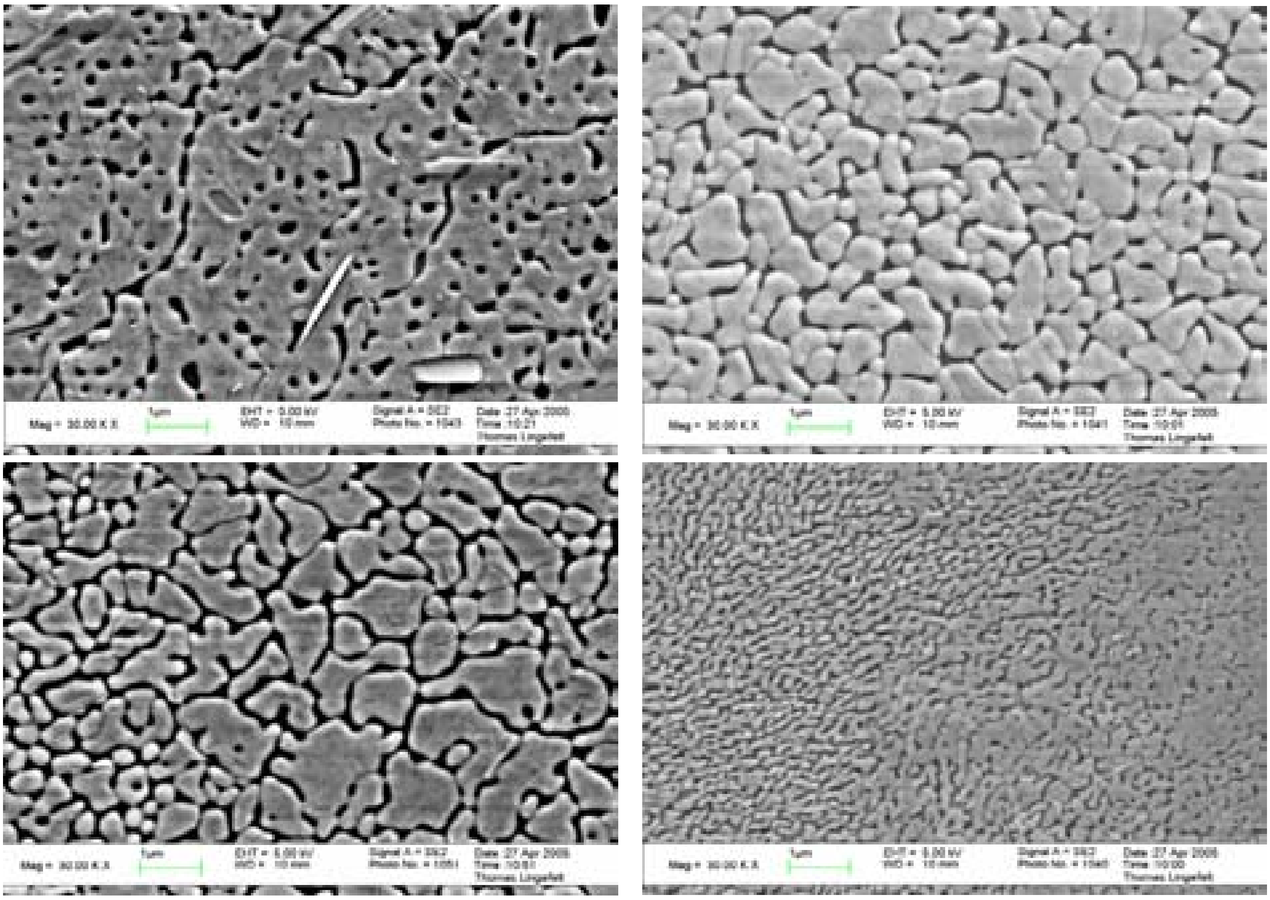


Fig.27 *Images showing different VO_2 surfaces. The upper images are undoped (sample A8 left and A9 right) and the lower images are doped (sample A12 left and A23 right).*

4 Conclusions

VO_2 thin films were successfully synthesized by the sol-gel technique and were analysed by FTIR, XRD, SEM and XPS. The undoped films had a transition temperature of 68 °C which is in agreement with the results previously reported in literature. The transition temperature was modified by doping the VO_2 films with tungsten. Attempts were also made to dope the films with rhenium but proved unsuccessful with the present method. The tungsten concentration in the films was varied from 1 to 4 at% and at best the transition temperature was lowered to 22 °C, *i.e.* a reduction by 46 °C, at a tungsten level of 4 at%. However the doping affects the transmittance in the semi-conductor state, making it poor with a doping concentration of tungsten over 1 at%. Theories about what happens when the film is doped were presented in section 1.1.1. The XPS analysis indicated that tungsten was present as W^{6+} in the VO_2 lattice. This goes in line with the theory presented by Burkhardt *et al.* except for the valence of the vanadium. When the VO_2 films were doped a reduction time of 2.5 h was not enough causing unreduced VO-phases to be formed. To avoid these phases the reduction time should be extended by at least 30 minutes. The rhenium was never incorporated into the VO_2 lattice because volatile Re-compound was formed, that was transported away from the film by the gas flow. It was not possible to compare either the impact of different valence or the type of co-ion since the rhenium doping did not succeed and the tungsten oxide (WO_3) did not dissolve in the isopropanol.

All substrates used in this project were prepared according to the RCA cleaning procedure. However at the end of the project two things were noted that need to be changed in the RCA procedure:

- The substrates should not be stored in water after the cleaning procedure, because it resulted in blotched surfaces.
- To avoid scratches and unevenness on the silica surface, the RCA cleaning procedure should be performed with only one substrate at a time or in a manner so that the substrates do not come into contact with each other.

5 Further work

Further work about the synthesis of VO_2 thin films and the effects of doping could be preformed. Examples of areas that need more attention are:

- **The aging process** – Although some positive effects where seen on the surface quality of the film when the vanadium containing sol was allowed to age in a cool environment the effects were not measured. Aging time *vs* film quality experiments could be performed, also the effects of warm or cold aging.
- **The reducing step in the furnace** – What is the optimal temperature in the furnace for the reducing process of the V_2O_5 film; doped or undoped? This question needs more work and further experiments. Pure VO_2 was never obtained in this work for doped VO_2 films. Also, can the H_2-Ar flow be increased to obtain the VO_2 phase more rapidly? How does the VO_2 film thickness influence the reducing time spent in the furnace?
- **Film thickness** – Transition temperature results for doped and undoped film should be set in relation to the thickness of the film.
- **Transition temperature –** Can the transmittance change at the transition temperature be larger, if so, how can this be accomplished? Figure 14 for the undoped VO_2 film shows that the transmittance is not max or min before and after the transition temperature. Can this be related to impurities, such as carbon, that was found in the XPS analysis? Or can it depend on other vanadium oxide phases? Carbon can be burnt away from the film in a preheating step in the furnace at 500 °C in vacuum, but this will, on the other hand result in a V_2O_5 network that needs up to 12 h to be reduced into VO_2.
- **Film durability –** How long will the VO_2, doped or undoped, film last in real situations? Can the film sustain acid rain, gasoline, endless temperature shifts, physical impact etc. when used on a vehicle for example?
- **Spin coat –** The settings used on the spinning machine in this project gave good V_2O_5 films. Even so, better films can be accomplished by tuning the spinning speed and spinning time with more experiments.
- **Rhenium doping –** A theory was presented in this report that Re was transported away with the gas flow in the reducing process as Re_2O_7, $ReCl_5$, $Re(CO)_x$ or in some other form. This theory can easily be confirmed by further experiments. If the theory is

true other methods for reducing the film needs to be tested, for example a 100 °C preheating step in vacuum? Perhaps a new method for synthesising the Re-doped VO_2 films needs to be developed?

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Appendix 1; Calculations

The following formula has been used to calculate the doping percentage of each dopant:

$$X_D = \frac{n_D}{n_V + n_D}$$

where X_D is the doping fraction in the sol, n_D is the number of moles of the doping compound and n_V is the number of moles of vanadium(V)oxytriisopropoxide. When the amount had been calculated it was multiplied with M (g/moles) to get the mass (mg) of dopant to use.

Calculations for vanadium(V)oxytriisopropoxide:

$$\rho_V = 1.035 g/ml$$

$$V_V = 3.5 ml$$

$$M_V = (12.001 * 9) + (1.008 * 21) + (15.999 * 4) + 50.94 = 244.11 g/mole$$

$$m_V = \rho_V * V_V = 1.035 * 3.5 = 6.6225 mg$$

$$n_V = \frac{3.6225}{244.11} = 0.0148396 moles$$

In table A:1 the mass of each dopant is listed.

Table A:1 *The mass of dopants that was used in the experiments.*

Dopant	**Percentage**	**m (mg)**
W^{6+} (WCl_6)	1 %	59.45
W^{6+} (WCl_6)	2 %	120.11
W^{6+} (WCl_6)	4 %	245.22
Re^{7+} (Re_2O_7)	2 %	146.70
Re^{5+} ($ReCl_5$)	2 %	110.09
Re^{5+} ($ReCl_5$)	6 %	344.31
Re^{5+} ($ReCl_5$)	12 %	735.57

Appendix 2; Sample specifications

Sample	**Rpm**	**Time (s)**	**Layers**	**Oven**	**Doping**	**Comments**
A1	2000	30	2	500 °C, 2 h		VO_2
A2	2000	20	2	500 °C, 2 h		Few VO_2 peaks
A3	2000	30	2	500 °C, 15 h		Over reduced
A4	2000	30	2	500 °C, 2 h		
A5	2000	30	2	500 °C, 2 h		Few peaks, no VO_2
A6	2000	30	2	500 °C, 2 h		Not so good, no VO_2
A7*			1	525 °C, 2.5 h		Lots of unreduced VO-peaks, some VO_2 peaks
A8	2000	30	2	525 °C, 2.5 h		VO_2
A9	2000	30	2	525 °C, 2.5 h		VO_2
A10	2000	30	2	525 °C, 2.5 h		VO_2
A11	2000	30	2	525 °C, 2.5 h		
A12	2000	30	2	525 °C, 2.5 h	2 % Re_2O_7	XRD-graph shows a distorted VO_2-pattern
A13	2000	30	2	525 °C, 2.5 h		
A14	3000	15	2	525 °C, 2.5 h	2 % Re_2O_7	VO_2
A15	3000	15	1	525 °C, 2.5 h	2 % Re_2O_7	The layer is too thin
A16	3000	15	1	525 °C, 2.5 h	2 % $ReCl_5$	The layer is too thin
A17	3000	15	1	525 °C, 2.5 h	2 % WCl_6	Not good, unreduced
A18	2000	30	2	525 °C, 2.5 h	2 % Re_2O_7	VO_2 + unreduced
A19	2000	30	2	525 °C, 2.5 h	2 % WCl_6	VO_2 + unreduced
A20	2000	30	2	525 °C, 2.5 h	2 % $ReCl_5$	VO_2 + unreduced
A21	2000	30	2	475 °C, 2.5 h		VO_2
A22	2000	30	2	525 °C, 2.5 h	1 % WCl_6	VO_2 + unreduced
A23	2000	30	2	525 °C, 2.5 h	4 % WCl_6	VO_2 + unreduced
A24	2000	30	2	525 °C, 2.5 h	6 % $ReCl_5$	Many peaks indicating unreduced V_2O_5 + some VO_2 peaks
A25	2000	30	2	525 °C, 3 h	12 % $ReCl_5$	Many peaks indicating unreduced V_2O_5 + some VO_2 peaks

** This sample was not spin coated. It was made by hand with only one thick layer to see if it would be possible to get rid of the hydroxide-bonds that appeared in the XRD graphs at values of* 2θ *around 12 to 16 .*

Characterisation methods performed on the samples:

Sample	Characterisation methods
A1	XRD, FTIR
A2	XRD
A3	XRD
A4	none
A5	XRD
A6	XRD
A7	XRD
A8	XRD, FTIR, SEM/EDX
A9	XRD, SEM, XPS
A10	XRD
A11	none
A12	XRD, FTIR, SEM/EDX
A13	none
A14	XRD
A15	XRD
A16	XRD
A17	XRD
A18	XRD
A19	XRD, FTIR
A20	XRD
A21	XRD
A22	XRD, FTIR
A23	XRD, FTIR, SEM/EDX, XPS
A24	XRD, FTIR
A25	XRD, FTIR, XPS

Appendix 3; RCA cleaning procedure

1. wash the substrates in deionized and ultrafiltered water in ultrasonic bath 3 times, each time with fresh water (1 minute each)
2. make up solution A (below); immerse the substrates and heat in Pyrex beaker on hot plate to 75-80 °C. Clean for ten minutes
3. rinse three times in deionized water and finally in the ultrasonic bath
4. make up solution B (below); immerse the substrates and heat in Pyrex beaker on hot plate to 75-80 °C. Clean for ten minutes
5. wash, ultrasonically in deionized filtered water five times, each with fresh water. Keep the substrates in deionized filtered water when the procedure is completed

A $5\ H_2O : 1\ H_2O_2 : 1\ NH_4OH$

B $H_2O : 1\ H_2O_2 : 1\ HCl$

APPENDIX 4; FLOW DIAGRAM FOR THE VO_2 SYNTHESIS PROCESS