ATMOSPHERIC PRESSURE
CHEMICAL VAPOUR DEPOSITION
OF VANADIUM OXIDES

by

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“There are no such things as applied sciences only applications of science.”

*Louis Pasteur, 1872*
The APCVD of vanadium(IV) oxide thin films from halide precursors was investigated. It was found that the phase of vanadium oxide obtained could be controlled by the reactor temperature and precursor ratio. For vanadium(IV) chloride and water, reactor temperatures > 550 °C and an excess of water over VCl₄ was required to produce VO₂ thin films. For vanadium(V) oxytrichloride and water, reactor temperatures > 550 °C and an excess of water over VOCl₃ also produced VO₂ but required low total gas flow rates (< 1 L min⁻¹) for complete coverage of the substrate.

Vanadium(IV) oxide thin films doped with metal ions (W, Cr, Nb, Ti, Mo or Sn) were also prepared by the APCVD process in order to reduce the thermochromic transition temperature (Tₜ) from 68 °C for the undoped material to < 30 °C. The most successful dopant was tungsten, introduced into the VOCl₃ and water system as WCl₆ which lowered Tₜ to 5 °C for a 3 atom% tungsten doped thin film. Tungsten(VI) ethoxide was introduced into the VCl₄ and water system and reduced Tₜ of VO₂ to 42 °C for a 1 atom% tungsten doped thin film. Chromium, introduced as CrO₂Cl₂, formed a chromium vanadium oxide that did not display any thermochromic properties. Niobium, introduced as NbCl₅ into the VOCl₃ system, reduced Tₜ of VO₂ but the amount of niobium introduced could not be easily controlled. Molybdenum, introduced as MoCl₅, also reduced Tₜ of VO₂, but the form of the molybdenum appeared to be different from that required for complete control of Tₜ. Titanium, introduced as TiCl₄, produced phase segregated films of VO₂ and TiO₂ with interesting multifunctional properties and a reduced Tₜ. Tin, introduced as SnCl₄, also formed a phase segregated material of VO₂ and SnO₂ with a slightly reduced Tₜ.
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1. Introduction.

INTRODUCTION

1.1 Introduction.
This thesis details the preparation and analysis of thin films of vanadium oxides on glass substrates from the atmospheric pressure chemical vapour deposition (APCVD) reaction of vanadium(IV) chloride with water and vanadium(V) oxytrichloride with water. The target material was thermochromic vanadium(IV) oxide, which has numerous technological applications due to its relatively low thermochromic transition temperature. The preparation of doped vanadium(IV) oxide films from the APCVD reaction of these vanadium precursors with precursors of tungsten, chromium, molybdenum, niobium, titanium and tin are also described. The thermochromic properties of the films were investigated to determine their potential use as intelligent window coatings.

Firstly, a discussion will be given of the motivations behind this research along with a brief description of solar control coatings, which are the target application. This will be followed by some of the properties of vanadium(IV) oxide that cause the thermochromic transition and how doping can affect the temperature at which this occurs, including a summary of the results of previous workers in the field of thin films of vanadium(IV) oxide. A description of how thin films of vanadium(IV) oxide have been prepared previously and an introduction to the processes involved in APCVD will also be given.

The experimental sections will consist of an examination of the production of pure and doped vanadium(IV) oxide thin films using APCVD and inexpensive, readily available precursors. The precursors chosen were chlorides and oxychlorides. Halide precursors are often overlooked in CVD systems in favour of metal-organic precursors, but can be useful for the CVD of oxide materials. The suitability of these films for intelligent window coatings prepared from these systems was tested by determining the thermochromic transition temperature and reflectance-
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transmittance properties below and above the thermochromic transition temperature.

1.2 Solar control coatings and motivations for this work.

The use of air conditioning systems to maintain comfortable working and living environments in recent times has become increasingly common. This leads to a dramatic increase in the use of electricity and a concurrent increase in carbon dioxide emissions and other atmospheric pollutants that are released in the electricity generation process. A self-propagating cycle results, in which global warming due to increases in these greenhouse gases necessitates the increased use of air conditioning systems. Technology is thus required that can reduce the use of air conditioning in commercial and residential buildings to help break this cycle.

Solar control coatings on windows are a technology that enables the windows in commercial or residential buildings to play an active role in the energy efficiency of the building. Currently available commercial products consist of an 'all-or-nothing' approach to solar control coatings. This means that where the environment is consistently hot, thin metallic coatings or tinted glass is used so that the solar heat is reflected away or prevented from entering the building, which reduces cooling costs. Where the environment is consistently cold, retention of heat within the building can be achieved by using a wavelength selective coating, such as tin doped indium oxide (ITO). ITO is visually transparent and has low emissive properties. This allows sunlight to enter the building generating blackbody radiation. The blackbody radiation, along with heat generated internally, is prevented from escaping the building and thus reduces the heating requirements of the building. A further development is the potential use of thermochromic coatings as intelligent window coatings. These change their optical properties with temperature, and are usually related to a structural phase change on passing through a critical temperature, \( T_c \). Thermochromic coatings would be applicable to climates where there are extreme changes in temperature over the year, for example central and northern Europe and the north east of the USA that have hot summers and cold winters.
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Vanadium(IV) oxide is one example of a thermochromic material that shows promise as an intelligent window coating. A pictorial representation of how a vanadium(IV) oxide thin film might work as an intelligent window coating is shown in Figure 1. The transition temperature for pure single crystalline vanadium(IV) oxide is 68 °C. At temperatures below $T_c$, the material is visually and infrared transparent. This allows most of the solar radiation to pass through the window maximizing the heating effect of the sunlight and black body radiation within the building, keeping the interior warm. At temperatures above $T_c$, the thermochromic coating becomes infrared reflective, preventing thermal radiation from excessively heating the building interior while remaining visually transparent, enabling the optimum use of natural light. Minimising the use of internal lighting also reduces building maintenance costs.

![Figure 1 Schematic demonstration of the application of thermochromic materials to advanced window glazing.](image)

The critical temperature of vanadium(IV) oxide, at 68 °C, is too high to maintain a comfortable temperature within a building (18 – 28 °C). The addition of impurities as dopants can influence the critical temperature of vanadium(IV) oxide, with tungsten having been shown to be the most effective dopant at lowering $T_c$ to about 25 °C in thin films prepared by physical vapour deposition methods and sol-gel spin or dip coating. A tungsten loading of only 2 atom% is required to reduce the thermochromic transition temperature of vanadium(IV) oxide thin films to room temperature.
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One distinct problem reported for vanadium(IV) oxide thin films for commercial glazing applications is the low luminous transmittance of the glazing film.\textsuperscript{10,12,13} This results in low visible light being transmitted by the window and the subsequent necessity for increased lighting to be used in buildings with the coating applied to the windows, which would negate any benefits due to the improved solar control. Two methods have been attempted to overcome the low luminous transmittance of vanadium(IV) oxide thin films. Granqvist\textsuperscript{4} attempted fluorine doping into the vanadium(IV) oxide lattice to form VO$_2$F$_y$ thin films by r.f. sputtering. This had the important property of reducing the thermochromic transition temperature along with increasing the luminous transmittance. Burkhardt \textit{et al.}\textsuperscript{10} however, described fluorine doping of vanadium(IV) oxide thin films as decreasing the sharpness of the thermochromic transition, reducing their usefulness in glazing applications.

A more promising solution to this problem is to apply an antireflection coating to the vanadium(IV) oxide thin film. Moon-Hee Lee \textit{et al.}\textsuperscript{12} investigated silicon(IV) oxide overlayers which greatly improved the luminous transmittance below and above the thermochromic transition temperature without affecting the temperature at which the transition occurred. A multifunctional window coating was prepared by Ping Jin \textit{et al.}\textsuperscript{13} who used titanium(IV) oxide as an antireflective coating over vanadium(IV) oxide thin films. They reported improved luminous transmittance and a reduced thermochromic transition temperature probably caused by strain or non-stoichiometry in the vanadium(IV) oxide thin film as uncoated vanadium(IV) oxide also displayed reduced thermochromic transition temperatures. The infrared switching contrast was reduced in the titanium(IV) oxide coated vanadium(IV) oxide thin films due to the reduced reflectivity of the composite films. It was proposed that the composite films would have multifunctional properties as titanium(IV) oxide is a well characterised photocatalyst\textsuperscript{14} in current commercial use as self-cleaning window coatings.\textsuperscript{15,16}

The problem with the luminous transmittance of vanadium(IV) oxide thin films is accentuated by the introduction of some dopants into the material and manifests as a decrease in the infrared transmittance of the low temperature, monoclinic phase of vanadium(IV) oxide with increasing dopant concentration. Tungsten doped
vanadium(IV) oxide thin films prepared by PVD showed decreasing infrared transmittance for the semiconducting phase as the tungsten content was increased. To enable vanadium(IV) oxide to be used as an intelligent window coating a method is required whereby thin films of the material are applied cheaply and efficiently to the glass during the manufacturing process in the float-glass furnace. Physical vapour deposition and sol-gel methods are processes that require the glass to be ready formed and cannot be integrated directly into a float-glass furnace, making them off-line processes. The ideal process for applying thin films of material to glass substrates is atmospheric pressure chemical vapour deposition, which has the advantage of not requiring a reduced pressure environment and has the high growth rates necessary for a high throughput process. These various methods are discussed in section 1.5 with their relevant advantages and disadvantages.

This project will examine and develop an APCVD method for the preparation of vanadium(IV) oxide thin films on glass substrates, using readily available precursors, for potential use as intelligent window coatings.

1.3 The structure and properties of vanadium(IV) oxide.

Since Morin firstly investigated the thermo-conductive properties of several transition metal oxides in the late 1950's, research has been undertaken to understand the nature of this transition and utilize these properties in various applications. The transition was named a metal-to-insulator transition due to the changes in conductive properties of the materials, but other properties of these materials soon became apparent and has since been e-labelled a metal-to-semiconductor transition (MST). Their optical properties also displayed discontinuous behaviour with large decreases in transmittance and increases in reflectance on passing through the transition temperature. The most promising of the transition metal oxides investigated by Morin for technological applications is vanadium(IV) oxide. This material has a metal-to-semiconductor transition temperature of 68 °C, the closest to room temperature of any other thermo-transitive metal oxides. Vanadium(IV) oxide undergoes a reversible metal-to-semiconductor phase transition (MST) that corresponds to a
structural phase transformation from monoclinic to tetragonal.\textsuperscript{21} The low temperature, monoclinic phase has unit cell parameters $a = 5.7529$ Å, $b = 4.5263$ Å, $c = 5.3825$ Å and $\beta = 122.6020^\circ$. The structure involves $V^{4+}-V^{4+}$ pairing with alternate shorter (0.265 nm) and longer (0.312 nm) $V^{4+}-V^{4+}$ distances along the monoclinic $a$ axis. The high temperature phase has a tetragonal rutile type structure, cell parameters $a = 4.5540$ Å and $c = 2.8557$ Å, with equidistant vanadium atoms (0.288 nm) in chains of edge sharing $[VO_3]$ octahedra. On passing through the MST, the (100) planes of vanadium atoms in the monoclinic phase shift by 0.043 nm parallel to (001). This shift is sufficient to break the $V^{4+}-V^{4+}$ pairs to form a tetragonal phase allowing metallic conductivity.\textsuperscript{21} The nature of this transition is discussed in more detail in section 1.4. Figure 2 shows representations of the two phases of vanadium(IV) oxide, cell parameters are taken from Rogers.\textsuperscript{21} The diagram of the monoclinic phase displays the alternate $V^{4+}-V^{4+}$ pairs and the distortion of the vanadium atoms along the $a$-axis.

![Figure 2](image_url)

Figure 2. Representations of the structures of (a) monoclinic VO$_2$, with $V-V$ pairs indicated, and (b) tetragonal VO$_2$, viewed along the $b$-axis of the unit cell.

On passing through the transition temperature, electrical conductivity and infrared reflectivity increase dramatically. There is only a relatively small thermochromic effect in the visible region. This has lead to vanadium(IV) oxide being investigated, among other uses, as potential data storage media,\textsuperscript{12} an optical switch,\textsuperscript{22} and as an infrared modulator for missile guidance systems.\textsuperscript{3} It is as intelligent window
coatings that vanadium(IV) oxide may find its most beneficial application and this is the targeted use of the material in this investigation.

1.4 The nature of the metal-to-semiconductor transition in vanadium(IV) oxide.

Numerous theoretical studies have been undertaken to understand the details of the metal-to-semiconductor transitions in transition metal oxides and vanadium(IV) oxide in particular. Despite these studies, the metal-to-semiconductor transition is still not understood fully. The most useful theoretical discussion, from a chemists’ point of view, to explain the MST of vanadium(IV) oxide is that of Goodenough, who described the band structure of the two phases of vanadium(IV) oxide in terms of molecular orbitals.

Goodenough discussed the possibility of an antiferroelectric transition being the driving force for the MST in vanadium(IV) oxide. He initially constructed an energy level diagram for tetragonal vanadium(IV) oxide, Figure 3a, and then argued that V-V pairing becomes energetically stable on cooling after the rearrangement of the band structure in forming the monoclinic phase, Figure 3b. In this way, he argued that there are two transition temperatures, $T_\alpha$ due to the antiferroelectric distortion and $T_\varepsilon'$, due to the crystallographic distortion, which happen to be coincident for vanadium(IV) oxide. Goodenough concluded that the “...driving mechanism for the low-temperature distortion in vanadium(IV) oxide is the antiferroelectric component of the distortion... the transition temperature $T_\alpha$ is controlled by the entropy of the lattice vibrational modes and not by the thermal excitation of electrons into the antibonding bands.”

A more recent paper by Eyert, who used density functional theory and the local density approximation, corroborated Goodenough’s model as a Peierls-like instability.

The MST of vanadium(IV) oxide, when cycled between the low and high temperature phases, displays hysteresis behaviour. This indicates a first-order transition whereby some regions of the material have completed the transition and others have not. First-order transitions involve a latent heat and the energy of the
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transition cannot be instantaneously transferred between the material and the surroundings.

![Diagram of band structure scheme for tetragonal and monoclinic VO2 at the Fermi level (E_f) (adapted from Ref. 20). d₅ orbitals are due to V-V pairs resulting from overlap of dₓ²₋ᵧ² atomic orbitals.](image)

1.5 Doping of vanadium(IV) oxide.

1.5.1. The effect of doping in vanadium(IV) oxide.

As mentioned in section 1.2, the introduction of impurities at dopant levels can influence the temperature at which the metal-to-semiconductor transition occurs. How dopants introduced into the vanadium(IV) lattice cause this effect is even less understood than the details of the MST itself. There are various theories on the action of doping in vanadium(IV) oxide based on empirical observation and theoretical calculations.

It was observed that high valent metal ions, e.g. W⁶⁺ and Nb⁵⁺, when substitutionally doped into vanadium(IV) oxide, decrease the MST temperature of vanadium(IV) oxide considerably, as low as room temperature with ~2 atom% W⁶⁺. Low valent ions, e.g. Al³⁺ and Cr³⁺, were shown to increase the MST temperature. MacChesney and Guggenheim made the observation that dopants with an ionic radius smaller than V⁵⁺, or that created V⁵⁺ defects which were smaller than V⁵⁺, increased the MST temperature, while dopants with a larger ionic radius than V⁵⁺ caused a decrease in the MST temperature. They did not postulate an explanation for their observations however.
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A more involved discussion was given by Goodenough, who builds on the X-ray diffraction observations that a second semi-conducting phase is present in doped samples between the low-temperature monoclinic phase and the high-temperature tetragonal phase. For low-valent dopant ions, this second semi-conducting phase has an orthorhombic structure and for high-valent ions it has a rutile structure. He then explains various scenarios of doped vanadium(IV) oxide in accordance to his description of the MST.

Cations that cannot contribute to homopolar bonds but can participate through π bonding, e.g. Ti\(^{4+}\), decrease the crystallographic transition temperature \(T'_c\). Dopants that introduce electrons to the vanadium \(d\) bands, such as cations with a higher valence state than \(V^{4+}\) (e.g. Nb\(^{5+}\) or W\(^{6+}\)) or anions with a lower valence state than \(V^{4+}\) (e.g. F\(^-\)), reduce the antiferroelectric stabilisation of the low-temperature phase by introducing \(\pi^*\) electrons into the antiferroelectric state. This then reduces the antiferroelectric transition temperature, \(T'_c\). The additional electrons are often localised as discrete \(V^{3+}\) ions.

Low valent cations, e.g. Al\(^{3+}\), introduced into the vanadium(IV) oxide lattice stabilise the antiferroelectric distortion as they are more stable in lower anion coordination sites, such as those in monoclinic vanadium(IV) oxide with its distorted lattice. Chromium(III) would be expected to show the smallest effect due to having a high preference for octahedral co-ordination.

The work of Goodenough has been further confirmed by Tang et al., who investigated the oxidation states of vanadium and tungsten in \(W_{0.05}V_{0.95}O_2\) and \(W_{0.05}V_{0.95}O_2\) by EXAFS and magnetic susceptibility studies. They suggest the formation of \(V^{3+}-W^{6+}\) and \(V^{3+}-V^{4+}\) pairs in vanadium(IV) oxide on tungsten doping, in accordance with Goodenough’s theories on the stability of the antiferroelectric distortion. This theory was based on powdered samples prepared by solid-state reactions and may not be completely applicable to thin films.

1.5.2 Tungsten Doping

Of the dopants investigated so far in single crystals and PVD or sol-gel prepared thin films, tungsten has been found to reduce the transition temperature of vanadium(IV) oxide by the greatest extent and as such is the dopant that has been
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the focus of the most research. For all methods of preparation, vanadium(IV) oxide films containing ~2 atom% tungsten have been shown to have a thermochromic transition temperature of about 25 °C, the ideal transition temperature for intelligent window coatings.

1.5.3 Other Dopants

In addition to tungsten other metal ions, when introduced into the vanadium(IV) oxide lattice as dopants, have been shown to affect the metal-to-semiconductor transition temperature of vanadium(IV) oxide. As discussed in section 1.5.1, the direction and magnitude of the change in the transition temperature can be related to a number of factors. Sol-gel methods for the formation of thin films of vanadium(IV) oxide have seen the greatest variety of dopant ions used with most of the first row transition metals having been used. Other metal ions have also been doped into the vanadium(IV) oxide lattice by sol-gel methods, including gold, molybdenum, niobium, and aluminium. The co-doping of molybdenum and tungsten, or tungsten and titanium into the vanadium(IV) oxide lattice have also been shown to give very low thermochromic transition temperatures. Tungsten and titanium co-doping of vanadium(IV) oxide displayed almost no hysteresis width for the infrared switching.

The range of metal ions that have been doped into the vanadium(IV) oxide lattice using PVD methods is not quite so extensive as with sol-gel and have mostly been limited to those that are known to induce the largest decrease in the metal-to-semiconductor transition temperature, namely tungsten, and molybdenum. Iron doping of vanadium(IV) oxide by PVD showed a minimum thermochromic transition temperature with 1.4 atom% Fe at 59 °C on the heating cycle.

Vanadium(IV) oxide film doped with 1.2 atom% fluorine (fluorine replacing oxygen atoms) has been shown to reduce $T_v$ to 20 °C, but also causes the hysteresis width of the thermochromic transition to broaden appreciably making fluorine doping unsuitable for window coating. The co-doping of tungsten and fluorine by PVD into vanadium(IV) oxide gave thin films with reduced thermochromic transition temperature and with improved visible transmittance over tungsten doped vanadium(IV) oxide.
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1.6 Film stresses and their effect on the thermo-chromic transition of vanadium(IV) oxide.

Pure, crystalline vanadium(IV) oxide displays a metal-to-semiconductor transition at 68 °C. Most thin films of the material also display the transition at the same temperature. There have been reports in the literature where thin films of pure vanadium(IV) oxide grown by various methods have shown transition temperatures lower than 68 °C. Maruyama et al. link the variations in the thermo-chromic transition temperature to the thickness of the thin film, but does not suggest a mechanism for the effect. Case however, investigated the effects of mismatches in substrate-film expansion co-efficients that cause extrinsic stresses in the film crystallites. He also used low-energy ion bombardment to cause intrinsic stresses in the thin film. Both effects were shown to decrease the temperature at which the MST occurs. Rakotoniaina et al. also discussed the effects of strain on the MST of vanadium(IV) oxide caused by pressure and tungsten doping, showing that pressure along the square plane of the rutile cell can result in a decrease in the thermo-chromic transition temperature.

1.7 Methods of preparing pure and doped vanadium(IV) oxide films.

Single crystals of vanadium(IV) oxide are unsuitable for many of the technological applications mentioned in section 1.3 and thin films of the material are required. Thin films also survive the stresses caused in cycling between the two polymorphs of vanadium oxide involved in the MST, which is known to cause single crystals to crack and disintegrate after only a few cycles. Guzman et al. showed that a vanadium(IV) oxide thin film prepared by sol-gel methods could be cycled $10^8$ times without any degradation in electrical contrast. The preparation of vanadium(IV) oxide thin films has proceeded using three routes, sol-gel spin and dip coating, physical vapour deposition (PVD) and chemical vapour deposition (CVD). Of these CVD has attracted less interest due to the inherent difficulty in achieving controllable stoichiometry using this method. Thin films of vanadium(IV) oxide prepared by PVD methods are generally used for fundamental studies of the properties of the thin films, whereas sol-gel spin or dip coated takes a more application based approach. Chemical vapour deposition studies also fall into the
latter category, with the ability to prepare thin films of vanadium(IV) oxide for commercial applications often being the focus of the research.

1.7.1. The sol-gel method.

The sol-gel method involves forming thin films by dip or spin coating substrates with solutions of metal alkoxides. The coatings are then suitably treated to form a thin film of the required metal oxide. The sol-gel methods are thus multi-stage, off-line processes. For the formation of vanadium(IV) oxide this involves partially hydrolysing the initial coating and then heating it in a reducing atmosphere to form crystalline vanadium(IV) oxide. The control of the thickness of the film is easily achieved by the addition of extra layers. Dopants are readily introduced by the addition of salts or alkoxides to the precursor solution in the necessary proportions. Due to the simplistic nature of the method, sol-gel has been used extensively to prepare vanadium(IV) oxide thin films in a pure and doped form. The most widely used precursor for the sol-gel preparation of vanadium(IV) oxide is vanadyl (iso-propoxide), followed by vanadyl tri(tert-amylalcohol). The alkoxide is usually dissolved in the parent alcohol to form the sol. Using different alcohols will cause transesterification and the formation of different alkoxides. The whole of the first row d-block elements and much of the second and third row d-block elements have been doped into vanadium(IV) oxide using this method.

A new method using polyvanadate sols was reported by Takahashi et al that used metallic vanadium dissolved in 30% H_2O and then heated to form a hydrosol. The hydrosol could then be spin coated onto a suitable substrate and reduced in a hydrogen atmosphere. Tungsten and molybdenum could be introduced in metallic form at the initial dissolution stage.

1.7.2 Physical vapour deposition methods.

The second general method discussed here involves physical vapour deposition (PVD) techniques. These involve energetically removing atoms or molecules from a target under reduced pressure conditions. The species can then react with any seed gases present in the deposition chamber to form a thin film of the desired compound by condensing onto a substrate. The composition of the thin film can be
accurately controlled by the amount of material removed from the target and the amount of reactive gas present in the deposition chamber. There are numerous ways to energetically remove atoms from a metal target and most have been used to prepare vanadium(IV) oxide thin films. These include laser ablation, RF magnetron sputtering, DC magnetron sputtering and ion beam sputtering. Doping is also readily achieved by placing another target in the deposition chamber. The amount of doping can be easily controlled by the relative sizes of the targets.

1.7.3 Chemical vapour deposition methods.
The final method used to prepare thin films is chemical vapour deposition, which is the method of choice in this project. The details of atmospheric pressure chemical vapour deposition are discussed in section 1.8 and will not be elaborated on here. As discussed in section 1.2, APCVD is the ideal method for producing thin films on high throughput glass substrates.

Doped vanadium(IV) oxide thin films prepared by CVD methods have not been reported in the literature. Pure vanadium(IV) oxide films have been produced by chemical vapour deposition onto glass substrates. Vanadyl tri(iso-propoxide) or vanadyl tri(iso-butoxide) have been used as single source precursors for the CVD of vanadium(IV) oxide films, usually by reducing the resultant vanadium(V) oxide thin films. Vanadium oxides can also be deposited using VCl₄ or VOCl₃ and an oxygen source such as water or ethanol or with carbon dioxide. These films can then be reduced to vanadium(IV) oxide in a suitable atmosphere. Vanadium(IV) oxide thin films have also been prepared from vanadium(III) acetylacetonate, V(acac)₃, by an APCVD method followed by slow post-deposition cooling, and from vanadium(IV) acetylacetonate, V(acac)₆, by a pyrolysis method in a controlled atmosphere. Vanadyl acetylacetonate, VO(acac)₂, has been used to prepare the metastable VO₃(B), which can be converted to the tetragonal phase by annealing in argon at 500 °C. Vanadyl precursors have also been used in a CVD method to prepare various vanadium oxide thin films including vanadium(IV) oxide. The precursors used in these studies are generally expensive and require a post-deposition reduction process to form vanadium(IV) oxide thin films. Ideally a
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A process is required that utilises inexpensive, readily available precursors that will produce vanadium(IV) oxide directly without the need for a reduction step.

1.7.4 Advantages and disadvantages of each method.

Sol-gel methods are simple to use, with readily available, though expensive precursors and give films with complete coverage of the substrate and even thickness. They are not, however, suitable for integrating into the industrial float-glass process as sol-gel techniques often involve spin coating the substrate, a process that is not easy with very large areas of glass.

PVD methods require reduced pressure or vacuum conditions and expensive evaporation/sputtering/ablation equipment. This would increase production costs, limiting the commercial applications due to economic factors. Growth rates are also often low with PVD techniques making them additionally unsuitable for integration into modern float glass processes.

Glass manufacturers currently use sol-gel and PVD methods to prepare coated-glass products but the extra cost of these off-line processes can make them prohibitively expensive for widespread, consumer use.

Atmospheric pressure CVD equipment can be easily integrated into the float-glass production process, the coaters are easily constructed and no expensive vacuum systems are required. The precursors are often readily available and relatively inexpensive, especially when films of only a few hundred nanometers may be required. Growth rates are also high compared to PVD techniques and are sufficiently fast to be suitable for float-glass production lines. These factors make APCVD methods the most attractive when wishing to prepare coated float-glass.

1.8 Atmospheric pressure chemical vapour deposition.

1.8.1 Processes involved in chemical vapour deposition.

Atmospheric pressure chemical vapour deposition (APCVD) is a technique used to deposit thin solid films from gaseous precursors onto a suitable substrate. The APCVD process is shown schematically in Figure 4. There are several steps associated with the CVD process (not always in this order):^50

Transport of the reactive species to the reaction site.
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Gas phase reaction.
Adsorption onto the substrate surface
Nucleation on the substrate surface.
Reaction and desorption of by-products
Film growth.

In the APCVD experiment the reaction chamber is at or near atmospheric pressure. The precursors therefore need to be low-melting solids or volatile liquids and are transported to the reaction site via hot, inert carrier gas. The substrate temperature also needs to be relatively high to initiate the deposition of the film.

1.8.2 Reaction sites in the APCVD process

In the reaction chamber two types of reaction may occur; homogeneous reactions occurring entirely in the vapour phase and heterogeneous reactions that occur at the vapour - solid surface interface.\(^6\) In cold wall reactors such as used in this project, homogeneous reactions and heterogeneous reactions at the reactor walls are suppressed due to the lower heat input to the system. Vapour - substrate reactions are therefore more important.\(^6\) Little is known about these types of reaction due to the difficulties in determining the exact nature of the surface species and the influence of the electronic structure of the solid surface on the kinetics of the reaction.
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1.8.3 Film growth mechanisms.
Three mechanisms describe the ways in which a film can grow on a substrate and are illustrated in Figure 5. The Volmer-Weber mechanism (Figure 5a) involves nucleation followed by three dimensional island growth. This mechanism occurs when the film's atoms are more strongly bound to each other than to the substrate. The Frank-van der Merwe mechanism (Figure 5b) proceeds in a layer-by-layer fashion due to the film's atoms being more strongly bound to the substrate than to each other. The Stranski-Kastanov mechanism (Figure 5c) is intermediate to the other two mechanisms, after one or two monolayers further growth is in the form of islands.

![Figure 5. Growth mechanisms for thin films.](image_url)

1.8.4 The rate of film growth.
The rate at which the film grows is partially determined by whether the process is vapour phase mass transport or surface kinetic controlled. Vapour phase mass...
transport controlled growth is limited by the rate at which reactants can be delivered to the substrate surface. Surface kinetic controlled growth is limited by the rate of decomposition of reactants on the substrate surface. The relationship between growth rate and temperature is shown in Figure 6. At very high temperatures growth rate may even decrease due to the depletion of reactants and/or an increase in the rate of desorption. 

To reach the substrate surface the precursors cross a boundary layer from the bulk, continuum flow. The continuum flow regime is active in CVD reactors when the ratio of the gas mean free path to characteristic reactor dimension (Knudsen number, \( K_n \)) is much less than unity (\( K_n << 1 \), as in APCVD reactors). The boundary layers form due to variations in species concentration, gas temperature and gas velocity as the gas passes across the hot substrate in the CVD reactor. Typical profiles for a horizontal, cold wall reactors are shown in Figure 7. As the gas encounters the substrate, frictional forces decrease the velocity of the gas close to
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the substrate surface. The concentration of the precursor also decreases along the substrate due to surface reactions. The temperature of the gas increases due to contact with the hot surface. The extent of the boundary layer determines how far along the substrate film growth occurs or whether a film forms at all.

Figure 7. Precursor concentration, gas velocity and temperature profiles for a cold wall, horizontal bed CVD reactor to illustrate boundary layers above the substrate during a CVD reaction.
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

Chapter 2

ATMOSPHERIC PRESSURE CHEMICAL VAPOUR DEPOSITION OF VANADIUM(IV) OXIDE.

2.1 Introduction.
A major objective of this project was to prepare single phase vanadium(IV) oxide thin films on glass substrates from readily available precursors using atmospheric pressure chemical vapour deposition. The simplest precursors for the chemical vapour deposition of transition metal oxides are the chlorides and oxychlorides. For many transition metals these compounds are liquids or volatile solids. These reagents are often highly reactive and will readily form oxides in contact with oxygen, water or other oxygen sources such as alcohols or esters. Alkoxide and acetylacetone compounds have also found use as single source precursors for the CVD of transition metal oxides. Again, they are volatile liquids or low melting solids that easily decompose to oxides at relatively low temperatures.

In this first experimental section of this thesis the production of vanadium oxides, especially vanadium(IV) oxide, from the APCVD reaction between vanadium(IV) chloride and water, and vanadium(V) oxytrichloride and water, will be described. Previous studies of the APCVD reaction of vanadium(IV) chloride and vanadium(V) oxytrichloride with water under APCVD conditions gave vanadium(V) oxide films. It was proposed that both precursors would give vanadium(IV) oxide if suitable conditions of precursor concentration and reactor temperature were obtained. The normalised ideal reactions for the formation of vanadium(IV) oxide from vanadium(IV) chloride or vanadium(V) oxytrichloride and water are given in Equations 1 and 2. Reactions to form other vanadium oxides (Equations 3 to 8) are also given. Standard enthalpies and entropies of formation of vanadium oxides were used to calculate the Gibbs free energy of the reactions using Hess’s Law and \( \Delta G = \Delta H - T \Delta S \).
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

\[ \text{VCl}_4 + 2 \text{H}_2\text{O} \rightarrow \text{VO}_2 + 4 \text{HCl} \]  
Equation 1

\[ \text{VOCl}_3 + \text{H}_2\text{O} \rightarrow \text{VO}_2 + 2 \text{HCl} + \frac{1}{2} \text{Cl}_2 \]  
Equation 2

\[ \text{VCl}_4 + 5/2 \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{V}_2\text{O}_3 + 4 \text{HCl} + \frac{1}{2} \text{H}_2 \]  
Equation 3

\[ \text{VCl}_4 + 3/2 \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{V}_2\text{O}_3 + 3 \text{HCl} + \frac{1}{2} \text{Cl}_2 \]  
Equation 4

\[ \text{VCl}_4 + 13/6 \text{H}_2\text{O} \rightarrow 1/6 \text{V}_5\text{O}_{13} + 4 \text{HCl} + 1/6 \text{H}_2 \]  
Equation 5

\[ \text{VOCl}_3 + 3/2 \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{V}_2\text{O}_3 + 3 \text{HCl} \]  
Equation 6

\[ \text{VOCl}_3 + \frac{1}{2} \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{V}_2\text{O}_3 + \text{HCl} + \text{Cl}_2 \]  
Equation 7

\[ \text{VOCl}_3 + 7/6 \text{H}_2\text{O} \rightarrow 1/6 \text{V}_5\text{O}_{13} + 7/3 \text{HCl} + 1/3 \text{Cl}_2 \]  
Equation 8

Thermodynamic calculations of Gibbs free energy for the reactions given in Equations 1-8 show that from vanadium(IV) chloride the most stable product was likely to be vanadium(IV) oxide (Figure 8) and from vanadium(V) oxytrichloride the most likely product would be vanadium(V) oxide (Figure 9). From these calculations it can be seen that large changes in vanadium oxidation state, between reagent to product, are less likely to occur than reactions that maintain the oxidation state of the reagent in the product. It should be noted that the conditions present in CVD reactors are far from the ideal equilibria on which thermodynamic equations are based and they can only serve as a guide to the probable products obtained when the reactions are performed. Despite these limitations, thermodynamic analysis of the likely products must be the starting point for any new CVD reaction.60
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

![Graph](image1)

Figure 8. Gibbs free energy calculations for vanadium oxide phases from the reaction of VCl3 and water.

![Graph](image2)

Figure 9. Gibbs free energy change for vanadium oxide phases from VCl3 and water.

2.2 Experimental.

All APCVD experiments were performed on a custom built apparatus consisting of a horizontal-bed cold-wall reactor connected by an arrangement of stainless steel heated pipes and valves to two heated bubblers. Liquid or high vapour pressure solid precursors could be used. A syringe driver was attached to the plain-line gas flow for the introduction of a third precursor; water was introduced into the system.
in this manner. A schematic of the APCVD rig used is shown in Figure 10. Eurotherm controllers and RS type k thermocouples regulated all heaters on the apparatus. The actual temperature of the surface of the glass substrate was slightly lower than that of the carbon susceptor, temperature profiles for the glass substrate at various susceptor temperatures are given in the Appendix.

Two vanadium precursors were used, vanadium(IV) chloride (VCl₄, Aldrich, UK, 99 %) and vanadium(V) oxytrichloride (VOCl₃, Aldrich, Strem, Alfa Asar, 99 %). These were placed into bubbler 2 for their individual studies. Distilled water was injected into the plain line gas flow using a fixed rate syringe driver (1.33 cm/min). Changing the size of the syringe varied the amount of water introduced. The substrate was SiO₂ pre-coated glass (Pilkington, UK) 150 mm × 45 mm × 3 mm. The SiO₂ coating acted as barrier layer to prevent metal ions present in the glass from leaching into the vanadium oxide coatings. Sodium could be a particular problem for coatings on float glass as it has a high mobility and will readily form vanadate compounds that do not show any thermochromic properties. The glass substrate was cleaned before use by wiping with a tissue soaked with water, and then a propan-2-ol soaked tissue, then rinsing with propan-2-ol. The glass was then allowed to dry in air before mounting in the CVD reactor.

In order to calculate the amount of precursor entering the gas phase to be transported to the CVD reactor, Equation 9 is used.

Where \( a \) is the amount of material introduced (mol min⁻¹), \( V_p \) is the vapour pressure of the material at the temperature of the bubbler (mmHg), and \( F \) is the carrier gas flow-rate through the bubbler (L min⁻¹).

Once all temperatures had stabilised, the syringe driver valve was opened and the syringe driver switched on so distilled water was introduced into the plain line gas flow. Nitrogen was passed through the bubbler containing the precursors and the bypass valve was closed. Vapours of the precursors were seen to pass through the exhaust. After allowing the flow to stabilise for approximately 10-20 s the three-way
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

valve was switched to allow the precursor to pass into the mixing chamber and on to the reactor. Once the allotted reaction time was complete the three-way valve was switched to the exhaust, the bypass valve opened, the nitrogen flow through the bubbler closed and the syringe driver switched off. The reactor heater was turned off and the substrate was allowed to cool in an atmosphere of nitrogen. The substrate was removed from the reactor below 200°C. All samples were handled in air and stored in plastic bags.

Analysis of the resulting films consisted of UV/visible absorption, visible/IR reflectance-transmittance, Raman spectroscopy, scanning electron microscopy, energy dispersive analysis of X-rays, X-ray photoelectron spectroscopy, X-ray diffraction and scratch resistance and adhesion testing. Contact angle and the photocatalytic activity were measured on a selection of the films.

UV/visible spectra were obtained on a Thermospectronic Helios-α spectrophotometer between 300 and 1100 nm, visible/IR reflectance-transmittance measurements were performed on a Zeiss miniature monolithic spectrometer (range 380-1150 nm) and on a Hitachi U-4000 spectrophotometer (range 240-2600 nm). An aluminium temperature cell controlled by RS cartridge heaters, Eurotherm temperature controllers and k-type thermocouples were used to manipulate sample temperature. Sample temperature was measured by a k-type thermocouple taped to the film surface.

Raman spectroscopy was performed on a Renishaw 1000 spectrometer using a 632.8 nm laser excitation source at 2 mW and 50x magnification. A Linkam THMS600 variable temperature cell with a liquid nitrogen pump controlled the temperature of the sample. In order to illustrate the thermochromic properties of the VO$_2$ films, the heating stage temperature was set to increase at a rate of 3 °C / min until the required temperature was reached. The stage was then set to dwell for 10 minutes to ensure the film was also at the set temperature.

Surface and edge-on images were obtained on a Hitachi S-570 scanning electron microscope at 20 kV accelerating voltage or a Jeol JSM-6301F scanning electron microscope at 15 kV accelerating voltage. Energy dispersive and wavelength dispersive analysis of X-rays (EDX/WDX) were performed on a Philips XL30 ESEM at 20 kV accelerating voltage and using Inca software (Oxford instruments).
X-ray diffraction patterns of the films were obtained on a Siemens D5000 instrument using primary Cu Kα radiation at 1.5418 Å with a 1.5° incident angle or in 0-2θ mode. Diffraction patterns at different temperatures were obtained at station 2.3 of the CCLRC synchrotron radiation source at Daresbury, UK using 1.2981 Å radiation with a 1.5° incident angle. The temperature was controlled using the aluminium sample holder described above. X-ray photoelectron spectrometry was performed on a VG ESCALAB 2201 XL instrument using monochromatic Al Kα X-rays with the pass energy set to 50 eV. XPS data was analysed using CasaXPS software version 2.2.29.

2.3 Results and discussion.

2.3.1 Film preparation and characterisation.

2.3.1.1 APCVD of VCl₄ + H₂O.⁶⁹

The thin films deposited from vanadium(IV) chloride and water were concentrated in the hottest area of the reactor towards the central, leading edge region of the substrate. There was less deposition at the edges and towards the exhaust end of the substrate. These regions were cooler than at the leading edge suggesting that the
reaction maybe kinetically controlled. The phase of vanadium oxide found at the cooler areas of the substrate tended to be the non-stoichiometric VO\textsubscript{x} phase. In one instance, an area of V\textsubscript{2}O\textsubscript{13} was created. It was noted that in all areas of the substrate analysed, no mixed phase vanadium oxide regions were observed, only single-phase materials. One other anomalous result indicated that the VO\textsubscript{2}(B) phase had been created and not the typical monoclinic vanadium(IV) oxide expected; this could not be repeated. VO\textsubscript{2}(B) is a metastable form of vanadium(IV) oxide first identified by Theobold,\textsuperscript{70} which can be converted to the rutile phase of vanadium(IV) oxide on heating.\textsuperscript{71,72}

<table>
<thead>
<tr>
<th>Reactor temperature\textsuperscript{(c)} / °C</th>
<th>Gas phase amount VCl\textsubscript{4} / mol min\textsuperscript{-1}</th>
<th>Gas phase amount H\textsubscript{2}O / mol min\textsuperscript{-1}</th>
<th>Composition\textsuperscript{(d)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.0022</td>
<td>0.024</td>
<td>VO\textsubscript{2}(M)\textsuperscript{(e)}</td>
</tr>
<tr>
<td>550</td>
<td>0.0024</td>
<td>0.024</td>
<td>VO\textsubscript{2}(M)\textsuperscript{(e)}</td>
</tr>
<tr>
<td>525</td>
<td>0.0025</td>
<td>0.024</td>
<td>V\textsubscript{2}O\textsubscript{5}</td>
</tr>
<tr>
<td>500</td>
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<td>0.024</td>
<td>V\textsubscript{2}O\textsubscript{5}</td>
</tr>
<tr>
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<td>VO\textsubscript{x}</td>
</tr>
<tr>
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<td>0.0024</td>
<td>0.024</td>
<td>No film</td>
</tr>
<tr>
<td>600</td>
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<td>0.125</td>
<td>VO\textsubscript{2}(M)\textsuperscript{(e)}</td>
</tr>
<tr>
<td>600</td>
<td>0.0024</td>
<td>0.125</td>
<td>VO\textsubscript{2}(M)\textsuperscript{(e)}</td>
</tr>
<tr>
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<tr>
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<tr>
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<td>0.048</td>
<td>VO\textsubscript{2}(M)\textsuperscript{(e)}</td>
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<tr>
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<td>0.0065</td>
<td>0.048</td>
<td>VO\textsubscript{2}(M)\textsuperscript{(e)}</td>
</tr>
<tr>
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<td>0.0031</td>
<td>VO\textsubscript{x}</td>
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<td>0.0031</td>
<td>Very thin VO\textsubscript{x}</td>
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<tr>
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<td>0.0031</td>
<td>Very thin VO\textsubscript{x}</td>
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<tr>
<td>600</td>
<td>0.0055</td>
<td>0.024</td>
<td>VO\textsubscript{2}(M)\textsuperscript{(e)}</td>
</tr>
</tbody>
</table>

Table 1. Conditions used to prepared vanadium oxide thin films from the APCVD reaction between VCl\textsubscript{4} and H\textsubscript{2}O. \textsuperscript{(c)}Temperature of carbon susceptor, see Appendix. \textsuperscript{(d)}Determined by Raman and XRD. \textsuperscript{(e)}A secondary phase of VO\textsubscript{x} formed on the colder edges of the glass substrates either at the leading edge (ca 1 cm) or the side edge (ca 1 cm) of the coating. In no deposition was the VO\textsubscript{x} and primary phase observed to coexist in the same portion of the substrate.
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

A summary of the conditions and products for the films prepared from vanadium(IV) chloride and water are given in Table 1 and Figure 11. Precursor amounts introduced into the CVD chamber were determined by using Equation 9 or, for water, the amount introduced via the syringe driver. It was found that the ratios of the precursors were more important than their concentration in the gas flow in determining the composition of the deposited films. An approximately ten times excess of water over vanadium(IV) chloride was found to be the ideal conditions for vanadium(IV) oxide formation.

Vanadium(IV) oxide was predominantly produced at higher substrate temperatures when a slight excess of water over vanadium(IV) chloride was introduced into the system. At lower temperatures vanadium(V) oxide was formed. No films were formed below 450 °C or with very large excesses of one precursor over the other.

Figure 11. Conditions-Products chart for the APCVD reaction between VCl₄ and H₂O.
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

Typical Raman spectra obtained for VO₂, V₂O₅, VO₄ and V₆O₁₃ are shown in Figure 12. These match the literature spectra of Barreca et al. The Raman spectrum of vanadium(IV) oxide showed bands at 143, 192, 223, 261, 310, 390, 500, 595 and 612 cm⁻¹. The peak positions of the Raman bands agreed with literature spectra to within ± 2 cm⁻¹. All Raman bands for monoclinic vanadium(IV) oxide could be assigned to an A₂g mode, except the band at 261 cm⁻¹ which has been assigned to a B₁g mode and the band at 143 cm⁻¹ which was not assigned. The Raman bands at 595 and 612 cm⁻¹ were likely to result from stretching modes of the V-O-V bridging bonds, while the other Raman bands could be attributed to bending motions of the vanadium-oxygen bonds.

The Raman spectrum of vanadium(V) oxide showed bands at 101, 145, 195, 283, 303, 407, 481, 529, 704 and 996 cm⁻¹, which agreed with literature spectra to within ± 2 cm⁻¹. Vanadium(V) oxide has a layered structure consisting of edge and corner sharing VO₅ square based pyramids. Long vanadium-oxygen (2.79 Å) bonds hold the vanadium(V) oxide layers together. Each VO₅ pyramid contains a short V=O bond. The Raman band at 996 cm⁻¹ corresponded to the vanadyl (V=O) stretching vibration with the bending vibrations of this bond assigned to the bands at 407 and 283 cm⁻¹. The bands at 704 and 529 cm⁻¹ could be attributed to stretching modes of the V-O-V bridging bonds, with the bending motions of these bonds assigned to the bands at 481 and 303 cm⁻¹. The low frequency bands are associated with the lattice vibration of the layered structure.

The Raman spectrum of V₆O₁₃ was similar in appearance to that of vanadium(V) oxide. These oxides have similar structural units. The bands of the Raman spectrum of V₆O₁₃ appeared at 133, 277, 303, 420, 500, 552, 688, 787, and 941 cm⁻¹. The frequency of the Raman bands observed here were about 5 cm⁻¹ lower than those for single crystals reported by Julien et al., which may be due to a slight non-stoichiometry in the thin films prepared by APCVD, but agreed with the band positions reported by Barreca et al. The low frequency band at 133 cm⁻¹, could be assigned to a rigid-layer mode with B₁g symmetry. The high frequency band at 941 cm⁻¹ corresponded to the stretching mode of the terminal vanadyl (V=O) bond. The bands at 271, 303 and 420 cm⁻¹ were assigned as bending vibrations of the V-O
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

and bridging V-O-V bonds with the stretching vibrations of these bonds at 552 and 688 cm\(^{-1}\).

\(VO_x\) is a non-stoichiometric phase of vanadium oxide with an ill defined composition, \(2 < x < 2.5\), and is actually a collection of phases with similar structures, interconverted by defects.\(^5\)

![Figure 12. Typical Raman spectra for vanadium oxides obtained from the APCVD reaction of VCl\(_4\) and water. (a) monoclinic VO\(_2\); (b) V\(_2\)O\(_5\); (c) V\(_2\)O\(_4\); (d) VO\(_2\).](image)

A glancing angle X-ray diffraction pattern of a thin film of vanadium(IV) oxide is shown in Figure 13. All of the vanadium(IV) oxide patterns showed a reflection at 27.8\(^\circ\), corresponding to the (011) plane. A reflection at 37.1\(^\circ\), corresponding to the closely spaced group of reflections of the (202), (211) and (200) planes was often observed. A broad amorphous background peak was present due to the glass substrate. None of the XRD patterns of vanadium(IV) oxide films showed sufficient reflections for satisfactory cell parameters to be derived and Miller indices were assigned by comparison to literature patterns.
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

A glancing angle X-ray diffraction pattern for a vanadium(V) oxide thin film prepared from the APCVD reaction vanadium(IV) chloride and water is shown in
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

Figure 14. The strong reflection at 20.3° corresponded to the (001) reflection and was always observed in the XRD patterns of vanadium(V) oxide. A weaker reflection at 21.8° was often observed and corresponded to the (101) plane. As with the vanadium(IV) oxide thin films, insufficient reflections were observed for satisfactory cell parameters to be calculated and Miller indices were assigned by comparison to literature patterns.

The typical morphology of a vanadium(IV) oxide thin film prepared from vanadium(IV) chloride and water is shown in Figure 15, which shows a film with particles having a diameter of about 60 nm. Some of the particles have agglomerated to form larger particulates. This type of film may result from an island growth mechanism. This type of film morphology is congruent with films grown on highly nucleating substrates.

The use of organic solvents instead of water as the oxygen source was also investigated. Ethanol, methanol, acetone and ethyl ethanoate, were introduced in turn into the CVD reactor using the syringe driver. In all cases, the thin films produced were highly contaminated with carbon, as shown by Raman spectroscopy and EDX analysis. Raman spectroscopy showed strong bands at 1350 and 1595 cm\(^{-1}\) corresponding to graphitic carbon.\(^{40}\) The films showed no thermochromic properties. The temperature of the reactor was sufficiently high to cause decomposition of the solvent to carbon, which was then incorporated into the film.

Figure 15. SEM image of typical VO\(_2\) film prepared from the APCVD reaction of VCl\(_4\) and H\(_2\)O (1:7) at 600 °C.
The films produced from vanadium(V) oxytrichloride and water also gave different phases of vanadium oxide depending on the conditions used. A summary of the conditions used and products obtained from the APCVD reaction of vanadium(V) oxytrichloride and water are given in Table 2 and Figure 16. As can be seen from Figure 16, most conditions resulted in orange/yellow vanadium(V) oxide but at higher substrate temperatures and with a slight excess of water over the stoichiometric amount from Equation 2, reduced phases of vanadium oxide could be formed. The reduced phases occurred in two discernible areas. At the leading edge of the substrate a thick, green area consisting of a mixed phase of $V_2O_5$ and $V_5O_7$ was formed. Closer to the exhaust end of the substrate single phase, dark yellow vanadium(IV) oxide was formed. Varying the total gas-flow rate through the CVD reactor could control the relative amount of these two phases. A decrease in total gas flow rate while maintaining the precursor ratios decreased the size of the mixed phase $V_2O_5/V_5O_7$ region and enable the majority of the substrate to be deposited with vanadium(IV) oxide. When the total gas flow rates were reduced to below $1.0 \text{ L min}^{-1}$ the region of mixed phase $V_2O_5/V_5O_7$ covered only 1-2 cm of the substrate at the inlet end of the reactor. In all cases complete coverage of the substrate was achieved.

The films formed were progressively thinner towards the exhaust end of the substrate suggesting that the film growth may have been mass transport controlled. The thickness did not appear to be affected by the variations in temperature across the substrate, as those formed from vanadium(IV) chloride and water described in section 2.3.1.1 seemed to be, precluding the kinetic growth mechanism.

Raman spectra and XRD patterns for these three regions are shown in Figure 17-Figure 20. The Raman spectra again matched those reported by Barreca. The XRD patterns matched database patterns as shown in Figure 18 to Figure 20. The Raman spectrum for a vanadium(IV) oxide thin film prepared from vanadium(V) oxytrichloride and water (Figure 17a) showed bands at 193, 223, 309, 394, 499, 571, and 615 cm$^{-1}$. The position of the bands were $\pm 2 \text{ cm}^{-1}$ of the bands for a vanadium(IV) oxide film prepared from the APCVD reaction of
vanadium(IV) chloride and water. A strong fluorescent background was apparent on this spectrum for which there was no explanation.

The Raman spectrum (Figure 17b) for a film prepared from vanadium(V) oxytrichloride and water and determined by X-ray diffraction (Figure 18) to be a mixed phase $V_6O_{13}-V_2O_5$ thin film showed bands at 106, 144, 166, 200, 269, 284, 297, 407, 489, 528, 700, 849, 880, 936, 994, and 1035 cm$^{-1}$. The bands at 106, 144, 200, 284, 407, 489, 528, and 994 cm$^{-1}$ (labelled pink in Figure 17b) were the Raman bands of vanadium(V) oxide. The Raman spectra of $V_2O_5$ and $V_6O_{13}$ have similar band positions$^{77}$ and overlap of bands will occur in a mixed phase situation. The
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

band at 700 cm\(^{-1}\), when compared to Figure 17c, appeared to have a shoulder on the low wavenumber side. This was due to the band at 684 cm\(^{-1}\) for \(\text{V}_2\text{O}_3\). The same situation occurred for the band at 407 cm\(^{-1}\), with the \(\text{V}_2\text{O}_3\) band at 403 cm\(^{-1}\) causing broadening of the vanadium(V) oxide band. All bands that showed overlap of \(\text{V}_2\text{O}_3\) and \(\text{V}_4\text{O}_9\) are labelled in red in Figure 17b. The bands labelled in black at 166, 849, 880, 936, and 1035 cm\(^{-1}\), did not correspond to \(\text{V}_2\text{O}_3\) or \(\text{V}_4\text{O}_9\) and may have been due to a phase of vanadium oxide not detected in the X-ray diffraction pattern. These bands could not be matched to any of the published Raman spectra for other vanadium oxides (\(\text{VO}_2\), \(\text{V}_2\text{O}_3\), \(\text{V}_4\text{O}_9\)) so are, at present unassigned.

The Raman spectrum for a vanadium(IV) oxide thin film prepared from the APCVD reaction of vanadium(IV) oxytrichloride and water (Figure 17c) showed bands at 107, 146, 199, 284, 307, 407, 489, 531, 707, and 995 cm\(^{-1}\), which were \(\pm 2\) cm\(^{-1}\) of the band positions of a Raman spectrum for a thin film of vanadium(IV) oxide prepared from vanadium(IV) chloride and water.

![Figure 16. Conditions-Products for the APCVD reaction of VOCl\(_3\) and water.](image-url)
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

Figure 17. Raman spectra for thin films prepared from the APCVD reaction of VOCl₃ and water. (a) VO₂; 650 °C, VOCl₃:H₂O 1:3; (b) mixed phase V₂O₅-V₂O₃; 600 °C, VOCl₃:H₂O 1:7, red = broadened V₂O₃ due to overlap of V₂O₃ bands; (c) V₂O₅, 650 °C, VOCl₃:H₂O 2:1

Figure 18. X-ray diffraction pattern of mixed phase V₂O₅-V₂O₃ formed from the APCVD reaction of VOCl₃ and water (1:7) at 600 °C. Reflection marked * is assigned to the (011) reflection of monoclinic vanadium(IV) oxide. Also shown are literature match patterns for V₂O₅ (41-1426) and V₂O₅ (43-1050)
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

![X-ray diffraction pattern](image)

Figure 19. X-ray diffraction pattern of yellow VO$_2$ area of film prepared from the APCVD reaction of VOCl$_3$ and H$_2$O (1:3) at 650 °C. Also shown is a literature match pattern for VO$_2$(M).

![X-ray diffraction pattern](image)

Figure 20. X-ray diffraction pattern of V$_2$O$_5$ film prepared from the APCVD reaction VOCl$_3$ and H$_2$O (3.5:1) at 550 °C. Also shown is a literature match pattern for V$_2$O$_5$.

From the XRD patterns (Figure 18 to Figure 20) the films appeared to be crystalline with sharp, intense reflections. Figure 18 shows the XRD pattern for a mixed phase, V$_2$O$_5$/V$_2$O$_3$ film deposited at the leading edge of the substrate when a slight excess
of water over vanadium(V) oxytrichloride was used. Miller indices were assigned by comparison with literature patterns. A weak reflection at 27.8° due the (011) plane of monoclinic vanadium(IV) oxide was observed in the XRD pattern of the mixed phase deposit. As vanadium(IV) oxide was present further along the substrate, its presence in the partially reduced phase was not surprising.

The vanadium(IV) oxide films from vanadium(V) oxytrichloride showed two reflections at 27.8° and 57.5° corresponding to the (011) and (022) planes of the monoclinic phase, indicating that the films were potentially preferentially orientated on the substrate along (011). Significantly, no reflections due to other phases of vanadium oxide were observed, suggesting a single-phase material was deposited. The films consisting of vanadium(V) oxide showed no apparent preferential orientation and could be indexed to an orthorhombic unit cell with cell parameters 

\[ a = 11.5520 \text{ Å}, \quad b = 9.4779 \text{ Å}, \quad c = 4.9411 \text{ Å} \]

The and \( c \) cell parameters were significantly larger than those of the literature patterns \((a = 11.512 \text{ Å}, \quad b = 3.564 \text{ Å}, \quad c = 4.368 \text{ Å})\) and was probably a result of the limited number of reflections observed in the thin films that incompletely represented the vanadium(V) oxide lattice.

The morphology of thin films of vanadium(IV) oxide grown from vanadium(V) oxytrichloride and water is shown in Figure 21. The films from vanadium(V) oxytrichloride were denser and had a narrower range of particle sizes than those prepared from vanadium(IV) chloride and water. They showed what appeared to be 50 nm diameter rod-like particles and aggregates growing perpendicular to the substrate, which may account for the preferential orientation observed in the X-ray diffraction pattern.

The growth rate using vanadium(V) oxytrichloride was also considerably faster, typically 800 nm/min with vanadium(V) oxytrichloride and water but only approximately 400 nm/min with vanadium(IV) chloride and water. The difference in film growth rates between vanadium(V) oxytrichloride and vanadium(IV) chloride was simply due to vanadium(V) oxytrichloride having a higher vapour pressure than vanadium(IV) chloride. A greater amount of vanadium(V) oxytrichloride was introduced into the CVD reactor than the amount of vanadium(IV) chloride introduced into the reactor. This meant larger amounts of
reactive species were potentially available for film formation when vanadium(V) oxytrichloride was used instead of vanadium(IV) chloride and so thicker films were produced.

![Figure 21. SEM image of VO₂ thin film from the APCVD reaction of VOCl₃ and H₂O (1:3) at 650 °C.](image)

When organic solvents were used as the oxygen source, carbon was incorporated into the films and no thermochromic properties were observed.

2.3.1.3 COMMON PROPERTIES.

The films of vanadium(IV) oxide were all a dark yellow colour. Most films showed poor adhesion qualities, they could be scratched by a scalpel and removed by wiping with a tissue. Most of the films passed the Scotch tape test. The films deposited from vanadium(V) oxytrichloride and water displayed slightly better adhesion qualities than those prepared from vanadium(IV) chloride and water. The films prepared from vanadium(IV) chloride and water appeared to have a more particulate morphology than those prepared from vanadium(V) oxytrichloride and water, which were crystalline with a densely packed morphology. This may account for the difference in adhesion properties. All of the films were unaffected by organic solvents (toluene, propanone, IMS, dichloromethane) and water but were attacked by oxidising acids (2 mol dm⁻³ HNO₃) non-oxidising acids (2 mol dm⁻³ HCl) and alkali (2 mol dm⁻³ NaOH). The amphoteric nature of vanadium oxides is
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

well known for the bulk materials. The films displayed no significant superhydrophilic effect, after one hour of irradiation with a UV lamp (265 nm), by a contact angle measurement. A vanadium(IV) oxide thin film prepared from vanadium(IV) chloride and water gave a contact angle of 66.1 °, a vanadium(IV) oxide thin film prepared from vanadium(V) oxytrichloride and water gave a contact angle of 62.8 ° and a vanadium(V) oxide thin film prepared from vanadium(IV) chloride and water gave a contact angle of 66.1 °. A plain glass substrate gave a contact of 70 ° indicating no significant hydrophilic effect compared to a plain glass substrate. None of the films displayed photocatalytic activity as shown by the stearic acid test.

In order to further elucidate the composition of the vanadium oxide films and to obtain an insight into the oxidation states of the ions present, a selection of the films were submitted to X-ray photoelectron spectroscopy analysis. An analysis of the bulk of the film was obtained by argon ion etching. A broad range survey scan was used as a qualitative measure of the elements present in the film, and high resolution scans of the characteristic regions of these elements were used for the quantitative analysis and peak fitting.

For all vanadium oxide films, the elements present on the surface were determined to be vanadium, oxygen, carbon, silicon and nitrogen. Nitrogen was a surface contaminant adsorbed from the atmosphere and the inert gas used to fill the sample entry air lock to the ultra-high vacuum analysis chamber. Most of the contaminant was removed in the ultra-high vacuum but some may have remained due the particulate, high surface area morphology of the films. Carbon contamination could be attributed to atmospheric contamination, but the major source was saturated hydrocarbons from the oil diffusion pumps in the analysis chamber. The XPS signal due to surface carbon was used as a charge compensation reference peak when assigning binding energies to the regions of the XPS experiment. The surface contaminants could be removed by argon ion etching to reveal a clean film surface. The signal assigned to silicon was due to the glass substrate, the films contained pinhole defects exposing the glass substrate through the film. No chlorine contamination from the chloride precursors was detected by XPS in any of the vanadium oxide thin films.
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

Peak fitting analysis of the V2p\textsubscript{1/2} XPS peak of a thin film prepared from vanadium(V) oxytrichloride and water (gas phase molar ratio 1:3) and identified as vanadium(IV) oxide by Raman and XRD analysis, revealed that on the surface of the film some of the vanadium ions were V\textsuperscript{V}, due to surface oxidation, with the majority present as V\textsuperscript{IV}. As the surface layers were etched and the bulk of the film exposed, the oxidation state of the vanadium ions was determined to be V\textsuperscript{IV} with a binding energy of 515.6 eV, as shown in Figure 22, confirming the presence of vanadium(IV) oxide. The O1s XPS peak of this level could be deconvoluted to two components. The peak at 532.6 eV was assigned to oxygen bound to silicon in the glass substrate and a small amount of residual surface contamination of carbon containing species, probably CO\textsubscript{x}. The peak at 531.0 eV was assigned to oxygen bound to a transition metal ion, in this case oxygen bound to vanadium. The peak area ratio, corrected for elemental sensitivity factors to give atom\% values, of the V2p\textsubscript{1/2} to O1s (O-V) peak was calculated to be 1:2, confirming the composition as VO\textsubscript{2}. As the film was further etched away some V\textsuperscript{2+} became apparent with a lower V2p\textsubscript{1/2} binding energy of 515.0 eV. This was most likely due to the preferential removal of lighter elements, especially oxygen, during the sputtering process that resulted in reduced forms of vanadium being present in the films.

![Figure 22. Deconvoluted XPS spectrum of V2p-O1s region for vanadium(IV) oxide thin film prepared by the APCVD reaction of VOCl\textsubscript{3} and H\textsubscript{2}O (1:3) at 650 °C. — data.](image-url)
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(V) oxide

For a vanadium(V) oxide film, prepared at 500 °C from vanadium(V) oxytrichloride and water (gas phase molar ratio 3.5:1), only V\(^{5+}\) cations, with a binding energy of 517.1 eV, were observed on the surface layer and in the bulk (Figure 23). Some reduced species were observed after substantial etching due to preferential sputtering of oxygen. At the surface layers the O1s XPS peak could be deconvoluted to two components, one with a binding energy of 532.4 eV could be assigned oxygen bound to silicon from the glass substrate and to carbon-oxygen species contaminating the surface. The second, with a binding energy of 530.1 eV, was assigned to oxygen bound to vanadium. Corrected peak area ratios, giving atom\% values, for the V2p\(_{3/2}\) to O1s for vanadium(V) oxide were approximately 2:5 confirming the presence of vanadium(V) oxide. Again, this was the expected result and reinforces that the film comprised single phase vanadium(V) oxide.

![Figure 23. Deconvoluted XPS spectrum of the V2p-O1s region for a vanadium(V) oxide thin film prepared from the APCVD reaction of VOCl\(_3\) and H\(_2\)O (3.5:1) at 500 °C. — data](image)

X-ray photoelectron spectroscopy was also performed on a film at the leading edge of a substrate prepared at 600 °C from vanadium(V) oxytrichloride and water (gas...
phase molar ratio 1:7) and determined to be mixed phase \( V_2O_5 \cdot V_2O_3 \) by Raman and XRD analysis. This film was established to consist of vanadium ions in both the +5 and +4 oxidation states. The \( V^{5+} \) XPS peak had a binding energy of 516.9 eV and the \( V^{4+} \) XPS peak had a binding energy of 515.5 eV. The O1s XPS peaks close to the surface of the film could be deconvoluted to two peaks. A peak with a binding energy of 532.4 could be assigned to oxygen bound to silicon from the glass substrate and residual carbon-oxygen containing contaminants. A second O1s peak with a binding energy of 530.4 eV could be assigned to oxygen bound to vanadium. This again is the expected result as \( V_2O_5 \) contains only \( V^{5+} \) and \( V_2O_3 \) has \( V^{4+} \) and \( V^{5+} \) ions. From an analysis of the atom% ratios of the \( V^{4+} \) and \( V^{5+} \) ions the film consisted of approximately 25% \( V_2O_3 \).

All binding energy assignments were matched to literature and database values. The result of the oxidation state analysis suggests that if dopant metal ions are introduced into the vanadium(IV) oxide lattice it may be possible to determine the effect the dopant ions have on the oxidation state of the vanadium ions and what form the dopant material takes in the vanadium oxide film.

<table>
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<td>27.316</td>
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<td>2.236</td>
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</table>

Figure 24. Deconvoluted XPS spectrum of the O1s-V2p region of a mixed phase \( V_2O_5 \cdot V_2O_3 \) film prepared from the APCVD reaction of \( VOCl_3 \) and \( H_2O \) (1:7) at 600 °C. --- data

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2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

2.3.1.4 Deposition onto silicon substrates.

As mentioned in the introduction, thin films of vanadium(IV) oxide have potential uses in data storage and as infrared modulators in thermal imaging sensors and missile guidance systems. These applications require the deposition of vanadium(IV) oxide onto silicon wafers. Using silicon wafers supplied by QinetiQ, the deposition of vanadium(IV) oxide onto silicon was attempted using the two precursor systems discussed above. The starting point was the conditions found to prepare vanadium(IV) oxide on glass.

Using vanadium(IV) chloride and water as precursors and a substrate temperature of 600 °C, Raman analysis indicated that a thin film with a mixed phase of vanadium(V) oxide and vanadium(IV) oxide was produced (Figure 25). Bands were shown at 100, 142, 191, 221, 261, 281, 302, 393, 403, 486, 614, 699, and 992 cm⁻¹. A very strong, sharp band was observed at 518 cm⁻¹, along with the slightly weaker, broader bands at 301, 435, 620, 672, 823 and a group of bands between 943 and 980 cm⁻¹, all assigned to the silicon substrate. The remaining Raman bands could be assigned to the two vanadium oxides as shown in Figure 25. The Raman bands at 100, 142, 281, 302, 403, 486, 699, and 992 were all ± 2 cm⁻¹ of those of pure vanadium(V) oxide thin films prepared on glass substrates (Figure 17c). The band at 303 cm⁻¹ was broadened somewhat by the presence of the silicon band at 301 cm⁻¹ and the vanadium(IV) oxide band at 309 cm⁻¹. The bands at 191, 221, 261, 393, and 614 cm⁻¹ could be assigned to vanadium(IV) oxide, being ± 2 cm⁻¹ of those for vanadium(IV) oxide thin films on glass substrates (Figure 17a).

This result displayed how the nature of the substrate can influence the type of thin film produced. Certain substrates may provide different reaction pathways by having a variation in surface activation energy for some reactive species.
When the vanadium(V) oxytrichloride and water system was used, Raman analysis indicated that single phase vanadium(IV) oxide thin films were deposited at a substrate temperature of 650 °C and 600 °C (Figure 25). Raman bands at 144, 191, 222, 260, 307, 337, 388, 441, 499, and 614 cm\(^{-1}\) could all be assigned to vanadium(IV) oxide. The bands at 337 and 441 cm\(^{-1}\) were very weak and were not observed in spectra from thin films of vanadium(IV) oxide on glass substrates (Figure 17), but were observed in spectra from single crystals.\(^{73,74,76}\) Both bands were assigned to \(B_2\) symmetry modes.\(^{73}\) The band at 571 cm\(^{-1}\) was not obvious on the films deposited on silicon, this band is not always observed in spectra from single crystals.\(^{70}\) This may indicate a more stoichiometric or crystalline phase being produced on the silicon substrates from the APCVD reaction of vanadium(V) oxytrichloride and water. The ability to prepare vanadium(IV) oxide on silicon substrates is quite an important breakthrough and opens up further applications for the APCVD of vanadium(IV) oxide thin films from halide based precursors.
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

Figure 26. Raman spectrum of (a) vanadium(IV) oxide thin film on (b) silicon substrate, from the APCVD reaction of VOCl₃ and H₂O (2:1) at 650 °C.

Figure 27. SEM image of VO₂ thin film deposited on silicon from the APCVD reaction of VOCl₃ and H₂O (2:1) at 650 °C.

The morphology of the vanadium oxide films deposited onto a silicon substrate (Figure 27) was also distinct from that of films deposited onto glass. Scanning electron microscopy showed that 500 nm long rod-like particles with a diameter of 50 nm were deposited above a layer of island growth. The particles appeared
randomly orientated on the substrate. The layer of island growth directly on the substrate showed particles, approximately 10 nm in diameter.

2.3.2 Thermochromic properties of films deposited onto glass substrates.

The thermochromic properties of thin films of vanadium(IV) oxide deposited onto glass substrates were analysed in three ways; Raman spectroscopy, glancing angle X-ray diffraction and visible/IR transmittance-reflectance spectroscopy. The Raman spectra of vanadium(IV) oxide at different temperatures is shown in Figure 28. The room temperature and 50 °C spectra were those typical of the monoclinic phase of vanadium(IV) oxide, the 65 °C spectrum, a temperature just below the transition temperature, showed all bands greatly reduced in intensity. When the temperature was increased to 75 °C, which is above the transition temperature, all bands due to the monoclinic phase of vanadium(IV) oxide were gone and a new band at 555 cm\(^{-1}\) appeared. Investigations on single crystals\(^{33}\) revealed that the Raman spectrum of the high temperature phase of vanadium(IV) oxide consists of four very broad (widths of 100 cm\(^{-1}\)), weak bands at 240, 390, 510, and 625 cm\(^{-1}\) and were the contributors to the broad feature observed in the Raman spectrum of high temperature vanadium(IV) oxide thin films. The bands could be assigned to \(B\(_2\) (240 cm\(^{-1}\)), \(E\(_1\) (390 cm\(^{-1}\)), \(A\(_g\) (510 cm\(^{-1}\)), \) and \(B\(_3\) (625 cm\(^{-1}\))\) symmetry modes and compared to the positions of the Raman band of rutile titanium(IV) oxide\(^{33,34}\) at 143 cm\(^{-1}\) (\(B\(_2\)\)), 447 cm\(^{-1}\) (\(E\(_1\)\)), 612 cm\(^{-1}\) (\(A\(_g\)\)), and 826 cm\(^{-1}\) (\(B\(_2\)\)). On cooling back to 50 °C, the low temperature monoclinic vanadium(IV) oxide spectrum was again obtained, illustrating the reversibility of the transition.
The transition could be followed in more detail by concentrating on the two bands at 190 cm$^{-1}$ and 220 cm$^{-1}$ and increasing the temperature at 1 °C intervals. The results of this experiment are shown in Figure 29. The reason for the high temperature, tetragonal phase of vanadium(IV) oxide having very weak Raman bands is due to large broadening of the Raman bands as the metal-to-semiconductor transition is approached, which smears-out the spectrum. The reason why this is so is not yet fully understood, but is generally attributed to the strong electron-phonon interaction described in section 1.4.$^{80}$ However, the Raman spectrum of vanadium(III) oxide, which also displays a metal-to-semiconductor transition, does not undergo line broadening as the transition temperature is approached and displays Raman bands in the semiconducting and metallic states. This eliminates the possibility of electron-phonon interactions being the cause of the line broadening of vanadium(IV) oxide at the thermochromic transition temperature, assuming a similar antiferroelectric ordering mechanism can be used to describe the driving force of the metal-to-semiconductor transition in both oxides.$^{80}$
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

Figure 29. Raman spectra between 100 and 240 cm$^{-1}$ at different temperatures for a VO$_2$ film prepared from VOCl$_3$ and water (1:3) at 650 °C.

The same sample was also studied by glancing angle XRD at different temperatures. The (011) reflection of the monoclinic phase transforming into the (110) reflection of the tetragonal phase was particularly easy to observe, especially with the preferential orientation present in the thin films, and the results of this study are shown in Figure 30. The first order transition was well shown in this study, the monoclinic and tetragonal phases of vanadium(IV) oxide were both seen to be present as the transition occurred, indicating that different regions underwent the transition at different times. This was a result of the energy involved in the transition being unable to be instantaneously transferred between the system and the environment so mixed-phase regimes were observed. The transition temperature ($T_c$) was shown to be where the intensities of the reflections for the monoclinic (011) plane and the tetragonal (110) plane were approximately equal. This occurred at a temperature of 67 °C on the heating cycle, which agreed with values reported in the literature for single crystals$^{18}$ and thin films$^{36,42,33,91}$ of pure vanadium(IV) oxide. On the cooling cycle the transition occurred at 54 °C, illustrating the broad hysteresis of the thermochromic transition of the thin films of vanadium(IV) oxide.
One characteristic property of vanadium(IV) oxide that makes it a useful material for intelligent window coatings is the increase in infrared reflectance and decrease in infrared transmittance when the material transforms into the high temperature phase. This was investigated by transmission-reflection spectroscopy. The transmittance-reflectance spectra of a vanadium(IV) oxide thin film at room temperature and 70 °C are shown in Figure 31.

At room temperature, the film transmitted across most of the visible spectrum and into the infrared and did not reflect greatly at any wavelength. At 70 °C, the transmittance of the film decreased into the infrared and the reflectance increased into the infrared. This was a typical response of vanadium(IV) oxide and displays the applicability of vanadium(IV) oxide thin films to window coatings. Substantial savings could be incurred if a vanadium(IV) oxide thin film, applied to a window, prevented the majority of the thermal, infrared radiation from entering a building.
Figure 31. Transmittance - reflectance spectra at 21 °C and 70 °C for a VO₂ thin film prepared from the APCVD reaction of VCl₃ and H₂O (1:3.5) at 600 °C.

One interesting result obtained was for very thin films of vanadium(IV) oxide of less than 100 nm thickness. These showed a reduction in the typical thermochromic transition temperature from 68 °C for the undoped material to less than 40 °C for the very thin films. The Raman spectra of such a film at different temperatures is shown in Figure 32. At 21 °C Raman bands were observed at 193, 223, 386, 555, and 612 cm⁻¹, all typical of the monoclinic phase of vanadium(IV) oxide. The presence of the broad band at 555 cm⁻¹ suggested that the film was close to the transition point as this feature is observed in spectra of the high temperature phase of vanadium(IV) oxide. When the temperature of the film was increased to 30 °C the band at 555 cm⁻¹ becomes more distinct while the remaining bands decreased in intensity. At 40 °C the film showed only the Raman band at 555 cm⁻¹ indicating the transition point had been passed. When the film was cooled back to 30 °C the Raman spectrum of the monoclinic phase of vanadium(IV) oxide was observed.
The reason for this decrease in the thermochromic transition temperature was not clear but was probably a result of strain in the film particles as described in section 1.6. The films were too thin for satisfactory X-ray diffraction patterns to be obtained so strain induced shifts in the reflections could not be observed.

The reflectance-transmittance spectra of a 100 nm vanadium(IV) oxide thin film is shown in Figure 33. The thin film displayed high transmittance across the wavelength range as would be expected for a very thin film but the optical contrast between the low temperature, semiconducting phase and the high temperature metallic phase was quite low. There was only a 10% difference in the infrared transmittance between the two phases. The contrast in the reflectance spectra was also low; the thermochromic transition was only just measurable in the reflectance spectra.
2. Atmospheric Pressure Chemical Vapour Deposition Of Vanadium(IV) oxide

Figure 33. Reflectance-transmittance spectra below and above the thermochromic transition temperature of a 100 nm thick vanadium(IV) oxide thin film prepared from the APCVD reaction of VCl₄ and H₂O (1:7) at 600 °C.

2.4 Conclusions and further discussion.

It has been shown that thermochromic vanadium(IV) oxide can be prepared from the atmospheric pressure chemical vapour deposition reaction of vanadium(IV) chloride and water and vanadium(V) oxychloride and water. In the vanadium(IV) chloride and water system higher reactor temperatures (>550 °C) promoted the formation of vanadium(IV) oxide. Lower reactor temperatures (<550 °C) induced the formation of VOₓ (2 < x < 2.5), V₂O₃ and V₃O₅ (Figure 11). This may indicate that vanadium(IV) oxide was a kinetic product of the reaction. A fast reaction pathway may have existed at the higher reactor temperatures allowing the formation of vanadium(IV) oxide. At lower reactor temperatures, this pathway may not have been possible, promoting the formation of the thermodynamically stable vanadium(V) oxide or other vanadium oxides with oxidation states higher than +4. Vanadium oxides of slightly higher oxidation state than vanadium(IV) oxide were formed at the edges of the substrate, which were lower in temperature due to the cold-wall CVD experimental set-up. This can be a disadvantage of the cold-wall CVD apparatus. Reactor conditions and precursor systems are required that deposit films in the mass-transport limited regime of film deposition.
Films deposited on silicon from the APCVD of vanadium(IV) chloride and water comprised of a mixed phase of vanadium(IV) oxide and vanadium(V) oxide. This illustrated the role the substrate can have in determining the composition of the films deposited. Surface activation energies may be dissimilar on different substrates, which can change the reaction pathways and thus the products of the reactions.

For the vanadium(V) oxytrichloride and water precursor system the predominant phase formed was vanadium(V) oxide, which was deposited using reactor temperatures below 600 °C or with an excess of vanadium(V) oxytrichloride over water. This system has been used to deposit thin films of vanadium(V) oxide onto devices for use as gas sensors. When a substrate temperature of 600 °C or above was used with an excess of water over vanadium(V) oxytrichloride two areas with different compositions were deposited. A thick, dark green/blue area comprising of a mixed phase of V$_2$O$_5$ and V$_2$O$_3$ was formed nearest to the gas-inlet. Further along the substrate yellow films of vanadium(IV) oxide were formed. Adjusting the overall gas flow-rate through the reactor could alter the relative sizes of these two regions. By decreasing the total gas flow rate the vanadium(IV) oxide region could be made to completely cover the substrate. On silicon substrates, the APCVD reaction of vanadium(V) oxytrichloride and water produced single phase vanadium(IV) oxide.

A factor that may influence the formation of vanadium(IV) oxide over vanadium(V) oxide at higher temperatures is the melting point of the two oxides. Vanadium(V) oxide melts at 690 °C, whereas vanadium(IV) oxide melts at 1967 °C. The temperatures used in these experiments were approaching that of the melting point of vanadium(V) oxide and this may have prevented any vanadium(V) oxide adhering to the substrate. This phenomenon was observed by MacChesney et al when reducing vanadium(V) oxide films prepared from vanadium(V) oxytrichloride and CO$_2$. The authors found that at temperatures above 550 °C, well below the melting temperature of vanadium(V) oxide, the liquid oxide phase did not wet the substrate causing the film to separate into droplets. It may be possible that something similar is occurring in the films prepared by APCVD. The adsorbed vanadium(V) oxide species may be too mobile on the glass substrate causing
desorption, which could prevent a forming vanadium(V) oxide film from adhering to the substrate at temperatures above 600 °C.

The films of vanadium(IV) oxide demonstrated the thermochromic properties associated with single crystals of vanadium(IV) oxide as shown by variable temperature Raman spectroscopy and transmittance–reflectance measurements. This indicated that these films showed promise as intelligent window coatings. One factor against their use was the poor adhesion qualities of the films. A protective coating would have to be used over the vanadium(IV) oxide films, or the film would need to be within the cavity of a double-glazing unit. The films of vanadium(IV) oxide are also an undesirable yellow colour, so a colour compensation layer would need to be applied to shift the visible absorption spectrum of the film towards the red, making the film appear a more appealing blue colour.

The transition temperature of the pure vanadium(IV) oxide films, at 68 °C, is too high for most practical uses but very thin films of vanadium(IV) oxide did show a depression in the thermochromic transition temperature, probably caused by strain in the material. A 100 nm thin film of vanadium(IV) oxide showed a thermochromic transition temperature of less than 40 °C. The optical contrast in the reflectance and transmittance spectra below and above the transition temperature was not very large and may preclude any commercial use.

Tungsten doping has been shown to be an effective way to decrease the transition temperature of vanadium(IV) oxide thin films significantly in PVD and sol-gel studies. The APCVD of tungsten doped vanadium(IV) oxide is examined in Chapter 3.
Chapter 3

ATMOSPHERIC PRESSURE CHEMICAL VAPOR DEPOSITION OF TUNGSTEN DOPED VANADIUM(IV) OXIDE.

3.1 Introduction.
In chapter 2 it was shown that it is possible to prepare single phase vanadium(IV) oxide from vanadium(IV) chloride and water, and vanadium(V) oxytrichloride and water on glass substrates using an atmospheric pressure chemical vapour deposition reaction.

The transition temperature of pure vanadium(IV) oxide is too high, at 68 °C, for the commercial application of the material as an intelligent window coating. Thin films prepared using physical vapour deposition and sol-gel methods have shown that by doping tungsten into the vanadium(IV) oxide lattice the temperature at which the thermochromic transition occurs in vanadium(IV) oxide can be lowered significantly. With a tungsten content of just 2 atom% the thermochromic transition temperature can be lowered to room temperature, making the material much more commercially applicable.

As was mentioned in section 1.7.4, PVD and sol-gel methods are not entirely suitable for the high throughput glass manufacturing industry. Chemical vapour deposition is a much more attractive method for applying thin films to glass substrates in a continuous on-line process. The production of metal doped vanadium(IV) oxide thin films by chemical vapour deposition has not previously been reported and this would be a natural progression in the development of commercial products.

This chapter will discuss the production of tungsten doped vanadium(IV) oxide thin films on glass substrates using two precursor systems. Firstly deposition from vanadium(IV) chloride, water and tungsten(VI) ethoxide will be described, followed by vanadium(V) oxychloride, water and tungsten(VI) chloride.
3. APCVD of tungsten doped vanadium(IV) oxide

The two tungsten precursors were investigated due to their potential to deposit tungsten oxide thin films in chemical vapour deposition systems. Tungsten(VI) ethoxide is a low melting solid that has been used as a single-source precursor to tungsten(VI) oxide films under atmospheric pressure CVD conditions, so should be suitable for doping tungsten into vanadium(IV) oxide using the apparatus used in this study.

Tungsten(VI) chloride is also a relatively high vapour pressure solid, but has not been reported as a CVD precursor to tungsten oxide thin films. Regragui et al. have described the use of tungsten(VI) chloride to deposit tungsten(VI) oxide using a spray pyrolysis method. Workers in the Parkin group have used tungsten(VI) chloride as a precursor for the atmospheric pressure chemical vapour deposition of tungsten(IV) sulfide. The CVD reaction between tungsten(VI) fluoride with water and other oxygen sources has been used to prepare tungsten oxide thin films so tungsten(VI) chloride can potentially be used as a precursor for the atmospheric pressure chemical vapour deposition of tungsten oxide films.

For each of the systems the introduction of different amounts of tungsten was attempted. The effect the amount of tungsten had on the metal-to-semiconductor transition temperature was investigated and the form that the tungsten ions take in the vanadium(IV) oxide lattice was elucidated.

In order to prevent the strain induced reduction of the thermochromic transition observed in very thin films (~100 nm) of vanadium(IV) oxide described in section 2.3.2, all films were deposited with a thickness of greater than 400 nm.

3.2 Experimental

Atmospheric pressure chemical vapour deposition experiments were performed in a similar manner to those described in section 2.2. The precursor used in the attempt to introduce dopant levels of tungsten into the vanadium(IV) oxide lattice was transferred to bubbler 1 and was transported to the CVD reactor together with the vanadium precursor and water.

Analysis of the doped vanadium oxide thin films consisted of X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), visible/IR
3. APCVD of tungsten doped vanadium(IV) oxide

reflectance-transmittance spectroscopy, and scanning electron microscopy (SEM). All instrumental analysis was performed on apparatus described in section 2.2. The thermochromic transition temperature of the films was determined by measuring the transmittance of the film at 2.5 μm on a Perkin Elmer 470 IR spectrometer while increasing the temperature of the sample by a rate of 2 °C/min using the aluminium heating-cell described in section 2.2, then allowing the sample to cool naturally. This wavelength was chosen because the thermochromic transition is greatest in the infrared so is easily measurable and will also give an indication of the effectiveness of the film in the target application by preventing heat carrying infrared radiation from being transmitted by the material.

3.3 Results and discussion.

3.3.1 Film preparation and characterisation.

In section 2.3.1 it was described how thin films of vanadium(IV) oxide could be prepared from the APCVD reaction of vanadium(IV) chloride and water with reactor temperatures above 550 °C and an approximately ten times excess of water over vanadium(IV) chloride. These conditions were used in an attempt to prepare tungsten doped vanadium(IV) oxide by introducing tungsten(VI) ethoxide into the CVD reactor along with vanadium(IV) chloride and water.

Tungsten(VI) ethoxide deposited a very thin blue film of tungsten oxide under the APCVD conditions required for the formation of vanadium(IV) oxide from vanadium(IV) chloride and water. The presence of tungsten in the film was confirmed by EDX and the Raman spectrum (Figure 34) showed a very broad band at low wavenumber and weak, broad bands at 807 and 947 cm⁻¹. The broad band at 807 cm⁻¹ is typical of monoclinic tungsten(VI) oxide. The broad band at 947 cm⁻¹ could be attributed to a stretching mode of terminal W=O bonds. The lack of any other Raman bands typical of tungsten(VI) oxide, which would be expected to be observed at 713, 270, and 131 cm⁻¹, was due to the non-stoichiometric and amorphous nature of the film; blue tungsten oxide is actually a slightly reduced form of WO₃ with the formula generally given as WO₃ₓ, where x is 0.8 to 1.0, whereas fully stoichiometric WO₃ is yellow.
3. APCVD of tungsten doped vanadium(IV) oxide

![Figure 34. Raman spectrum of tungsten oxide thin film deposited from the single-source APCVD reaction of [W(OCl)] at 550 °C.](image)

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<th>Phase from Raman and XRD</th>
<th>W atom% in film (±0.1%)</th>
<th>Transition temperature ± hysteresis width / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 - 180</td>
<td>550</td>
<td>0.0045</td>
<td>VO₂(M)</td>
<td>0.6</td>
<td>53 ±11</td>
</tr>
<tr>
<td>1.0 - 184</td>
<td>600</td>
<td>0.0047</td>
<td>VO₂(M)</td>
<td>0.6</td>
<td>53 ±12</td>
</tr>
<tr>
<td>1.0 - 185</td>
<td>600</td>
<td>0.0052</td>
<td>VO₂(M) and VO₂(B)</td>
<td>0.9</td>
<td>45 ±15</td>
</tr>
<tr>
<td>1.0 - 185</td>
<td>600</td>
<td>0.0049</td>
<td>VO₂(M)</td>
<td>0.8</td>
<td>49 ±15</td>
</tr>
<tr>
<td>1.2 - 189</td>
<td>650</td>
<td>0.0071</td>
<td>VO₂(M)</td>
<td>0.3</td>
<td>57 ±29</td>
</tr>
<tr>
<td>1.3 - 194</td>
<td>650</td>
<td>0.0088</td>
<td>VO₂(M)</td>
<td>1.2</td>
<td>42 ±16</td>
</tr>
</tbody>
</table>

Table 3. Conditions used in the APCVD reaction of VCl₄, H₂O and [W(OCl)] to prepared tungsten doped VO₂. Water was introduced at 0.048 mol min⁻¹. VO₂(B) was confined to the leading edge.

The films deposited from vanadium(IV) chloride, water and tungsten(VI) ethoxide had a similar visual appearance to the undoped vanadium(IV) oxide thin films described in section 2.3.1. X-ray diffraction and Raman spectroscopy were used to
determine the phase of vanadium oxide that was deposited while X-ray photoelectron spectroscopy was used to determine the amount of vanadium and tungsten present in the films. The results of these analyses are shown in Table 3. The films deposited were determined to be the monoclinic phase of vanadium(IV) oxide by X-ray diffraction and Raman spectroscopy. On one repeat run, the leading edge of the substrate gave an unexpected result, a region of the film with a width of about 1 cm was a dark blue colour and could be identified as VO$_2$(B) by X-ray diffraction, a metastable phase of vanadium(IV) oxide first characterised by Theobold.\textsuperscript{70} The film of VO$_2$(B) did not show any thermochromic properties in the temperature range investigated (<80 °C) and the result could not be repeated.

The amount of tungsten introduced into the vanadium(IV) oxide lattice was determined to be between 0.3 and 1.2 atom% by X-ray photoelectron spectroscopy. Due to the solid nature of the tungsten(VI) ethoxide precursor and its relatively low vapour pressure and low thermal stability, a tungsten amount of about 1 atom% seemed to be the maximum that could be doped using this particular precursor and therefore limited the lowest achievable thermochromic transition temperature to about 40 °C. The amount of tungsten introduced could be related to the conditions of the bubbler containing the tungsten(VI) ethoxide precursor. The highest flow rate and bubbler temperature (194 °C and 1.3 Lmin$^{-1}$) gave the highest amount of tungsten in the vanadium(IV) oxide film.

X-ray diffraction analysis revealed reflections at 26.9 °, 27.8 °, 36.8 °, 42.1 °. Insufficient reflections were observed for the calculation of accurate cell parameters but comparison with the literature enabled the assignment of the reflections to the (110), (011), (200) and (212) planes of the monoclinic phase of vanadium(IV) oxide as shown in Figure 35. Significantly, no reflections due to oxides of tungsten were apparent in any of the XRD patterns of the tungsten doped vanadium oxide films. This indicated that the tungsten was probably present as a solid solution in the vanadium(IV) oxide lattice, either interstitially or substitutionally. By comparison with database patterns there appeared to be no measurable shift in the position of the reflections from the undoped material. The ionic radius of tungsten(IV), tungsten(V) and tungsten(VI) cations are 0.66, 0.62, and 0.60 Å respectively\textsuperscript{6} which are not considerably larger than vanadium(IV) cations at 0.58 Å\textsuperscript{67} so any change in
3. APCVD of tungsten doped vanadium(IV) oxide

cell parameters caused by the introduction of tungsten ions into the vanadium(IV) oxide lattice would have been quite small.

![Graph showing XRD pattern](image)

**Figure 35.** XRD pattern of 0.6 atom% W doped VO₂ from the APCVD reaction of VCl₄, H₂O and [W(OC₃H₅)₆] at 600 °C. Also shown is a literature match pattern for VO₂(M).

Raman analysis was also performed on the tungsten doped vanadium(IV) oxide thin films. A Raman spectrum for a 1.2 atom% tungsten doped vanadium(IV) oxide thin film is shown in Figure 36. Raman bands were observed at 192, 222, 261, 307, 338, 390, 498, and 611 cm⁻¹. These bands were all in agreement with the line positions of the Raman spectrum of undoped vanadium(IV) oxide thin films prepared from vanadium(IV) chloride and water shown in section 2.3.1. The positions and line widths of the bands were not affected by the presence of tungsten in the vanadium(IV) oxide thin films.

As with the XRD pattern, bands due to tungsten oxide could not be observed in the Raman spectrum of tungsten doped vanadium(IV) oxide. The strongest band for tungsten oxide is at 807 cm⁻¹, which does not overlap with any of the vanadium(IV) oxide Raman bands. This band was not observed in the Raman spectra of tungsten doped vanadium(IV) oxide, suggesting that the tungsten oxide did not form a separate phase but instead formed a solid solution with the vanadium oxide.
3. APCVD of tungsten doped vanadium(IV) oxide

There also appeared to be very little broadening of the Raman bands of the tungsten doped vanadium(IV) oxide thin films compared to the undoped material. This again was expected as the low amount of tungsten present in the doped vanadium(IV) oxide thin films was small so any changes in polarisability of the bonds would only have a small effect on the appearance of the Raman bands.

Figure 36. Raman spectrum of 1.2 atom% W doped VO₂ thin film prepared from the APCVD reaction of VCl₄, H₂O and [W(OC₃H₅)₆] at 650 °C.

Figure 37. SEM of a 0.6 atom% W doped VO₂ thin film prepared from the APCVD reaction of VCl₄, H₂O and [W(OC₃H₅)₆] at 600 °C.
Scanning electron microscopy showed the morphology of the tungsten doped vanadium(IV) oxide films to be similar to that of thin films of undoped vanadium(IV) oxide (Figure 37), with particle aggregates of 100 nm in diameter. Edge-on SEM (Figure 38) showed the films to have a thickness of between 400 and 500 nm with a columnar growth structure of the Volmer-Webber type, typical of highly nucleating substrates.

Most of the films passed the Scotch tape test but could be easily removed by wiping with a tissue and could be scratched with a steel scalpel and a brass stylus. These results were similar to the undoped vanadium(IV) oxide films prepared from vanadium(IV) chloride and water and were related to the particulate nature of the films. The tungsten doped vanadium(IV) oxide films were unaffected by organic solvents and water but were attacked by acid and alkali, as with the undoped films. X-ray photoelectron spectroscopy was used to determine the elemental composition and oxidation states of the ions present in the tungsten doped vanadium(IV) oxide thin films. Survey spectra of the films indicated that the surface consisted of vanadium, oxygen, nitrogen, carbon and silicon, no tungsten was
observed on the surface of any of the tungsten doped vanadium(IV) oxide films prepared from vanadium(IV) chloride, water and tungsten(VI) ethoxide and none of the films were contaminated with chlorine. As with the undoped films, nitrogen was an atmospheric contaminant, while carbon could be attributed to atmospheric carbon dioxide and hydrocarbons from the oil diffusion pump in the vacuum chamber. Both of these contaminants could be removed from the surface of the film by argon ion etching. Depth profiling carried out by argon ion etching of layers of film material indicated that the tungsten appeared to be incorporated into the bulk of the film and was not present in the very uppermost surface layers (Figure 39). The contents of the tungsten ethoxide containing bubbler were checked after deposition. It was found that the tungsten precursor was not exhausted during deposition and no lines were blocked.

One possible reason for the bulk segregation of tungsten is related to the poor transport properties of tungsten(VI) ethoxide. When the three-way valves are closed at the end of a deposition experiment, tungsten(VI) ethoxide flow would cease immediately. Residues of vanadium(IV) chloride could still be transported to the reactor after the valves were closed and form a very thin layer of vanadium oxide.
over the tungsten doped film. This would give the results observed in the XPS depth profiling experiments.

Quantification was accomplished by integrating below the V2p, O1s and W4d3/2 XPS peaks. These peaks have no or minimal overlap of peaks due to other elements in the films giving much more reliable results. Peak fitting analysis was performed on the V2p3/2, O1s, V3p, and W4f peaks. Literature oxidation state assignments were more readily available for the W4f peaks than for the W4d3/2 used for the quantification.

Peak fitting analysis of the V3p, W4f peaks of the tungsten containing layers showed that the vanadium was predominantly present as V4+ with a V3p binding energy of 39.6 eV, and a reduced vanadium species with a binding energy of 37.9 eV which could be assigned to V3+. The assignment of vanadium oxidation states was confirmed by analysis of the V2p3/2 XPS peak. Two vanadium oxidation states were observed, a V4+ with a binding energy of 515.5 eV and V3+ with a binding energy of 513.6 eV. The presence of a reduced vanadium species was probably the result of the preferential sputtering of oxygen during the argon ion etching process and was the cause of the broadening of the V3p peak as the film was etched into the bulk material. The presence of reduced vanadium species could also be a result of tungsten doping as described in section 1.5.1, but this was difficult to confirm in these samples due to the bulk segregated tungsten, which was only detected after etching.

Peak fitting of the W4f XPS peaks gave one oxidation state for the tungsten ions. The W4f5/2 and W4f7/2 peaks had binding energies of 34.8 and 32.7 eV respectively. These corresponded to W4+ cations in WO2 indicating that the tungsten was present as W4+ in the tungsten doped vanadium(IV) oxide thin films. There was no broadening or position change of the tungsten peaks during etching that would have indicated the formation of reduced tungsten species due to preferential sputtering of oxygen. Tungsten may not have been affected to the extent of vanadium by the sputtering process due to its relatively low concentration in the films. This suggested that the tungsten undergoes a reduction reaction during deposition from the tungsten(VI) species of the precursor to the tungsten(IV) species in the vanadium oxide lattice. It should be recalled that the tungsten oxide
3. APCVD of tungsten doped vanadium(IV) oxide

thin films prepared using tungsten(VI) ethoxide as a single source precursor were of the blue, slightly reduced form of WO₃, indicating that reduced tungsten species are readily formed by the CVD of this precursor.

<table>
<thead>
<tr>
<th>Name</th>
<th>Pos.</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>W 2p</td>
<td>24.76</td>
<td>1.294</td>
</tr>
<tr>
<td>W 4f/2</td>
<td>32.72</td>
<td>2.131</td>
</tr>
<tr>
<td>V 3p (V⁺⁺)</td>
<td>39.58</td>
<td>4.238</td>
</tr>
<tr>
<td>V 3p (V³⁺)</td>
<td>37.85</td>
<td>1.736</td>
</tr>
</tbody>
</table>

Figure 40 Deconvoluted V 3p and W 4f XPS peaks for a 0.6 atom% W doped VO₂ thin film prepared from the APCVD reaction of VCl₃, H₂O, and [W(OCl₃H₅)₄] at 600 °C.

3.3.1.2 THERMOCHROMIC PROPERTIES.

The thermochromic properties of the tungsten doped vanadium(IV) oxide thin films prepared from vanadium(IV) chloride, water and tungsten(VI) ethoxide were examined by four methods. The Raman spectra and X-ray diffraction patterns of the films were measured at different temperatures to investigate the structural changes occurring during the transition. Also the optical properties (infrared hysteresis and reflectance-transmittance spectroscopy) were investigated at different temperatures to examine the suitability of the films for intelligent window coating applications.
3. APCVD of tungsten doped vanadium(IV) oxide

The Raman spectra of a tungsten doped vanadium(IV) oxide film at different temperatures is shown in Figure 41.

![Raman spectra at different temperatures for a 0.6 atom% W doped VO₂ thin films from the APCVD reaction of VCl₄, H₂O, and [W(OCl₄)[H₂]₂] at 600 °C.](image)

The changes in the Raman spectra of tungsten doped vanadium(IV) oxide as the temperature was increased followed the same pattern as for the undoped material. At room temperature the Raman spectrum showed bands at 192, 222, 307, 390, and 612 cm⁻¹. As the temperature was increased the intensity of the bands decreased and the bands broadened until they could not be observed. A weak, broad band was observed at 570 cm⁻¹ which could be related to non-stoichiometry in the vanadium(IV) oxide film and was observed in the undoped vanadium(IV) oxide thin films described in section 2.3.1.1. The spectra shown in Figure 41 are for a 0.6 atom% tungsten doped vanadium(IV) oxide film and the transition occurred at approximately 50 °C. It should be noted that no bands corresponding to tungsten oxide were observed in the Raman spectrum of the tetragonal phase of vanadium(IV) oxide reinforcing the observation that the tungsten formed a solid solution with the vanadium(IV) oxide lattice.

The structural change of the tungsten doped vanadium(IV) oxide could be followed by observing the (011) reflection of the monoclinic phase converting to the (110)
3. APCVD of tungsten doped vanadium(IV) oxide

reflection of the tetragonal phase. When compared to the pattern of the undoped vanadium(IV) oxide, no difference in the positions of the peaks was observed. The transition on the heating cycle occurred at 58 °C for the 0.3 atom% W doped vanadium(IV) oxide thin film, 10 °C lower than that of the undoped material.

![XRD of the monoclinic (011) reflection transforming to the (110) tetragonal reflection for a 0.3 atom% W doped VO₂ thin film prepared from the APCVD reaction of VCl₄, H₂O and [W(O₂CΗ₂)]₄ at 650 °C.](image)

To determine the thermochromic transition switching temperature, the transmittance of the films at 2.5 μm was measured while the temperature was cycled through the metal-to-semiconductor transition. The results of some of these measurements are shown in Figure 43. As the temperature was increased and the thermochromic transition temperature was approached, the transmittance of the films decreased dramatically. The thermochromic transition temperature decreased to as low as 45 °C for a vanadium(IV) oxide thin film doped with approximately 1 atom% tungsten (Figure 43c). This was in agreement with the changes observed in tungsten doped thin films prepared from PVD and sol-gel methods. A typical contrast between the low temperature transparent state and the high temperature reflective state was 25 % and was not affected by the amount of...
tungsten present in the material. The transmittance of the low temperature, semiconducting phase decreased with increasing tungsten content, again in accordance with observations from PVD prepared tungsten doped vanadium(IV) oxide thin films. As the amount of tungsten in the films increased the hysteresis width also increased, possibly due to the number of defects in the vanadium(IV) oxide lattice which would cause a greater variation in the temperatures at which different regions of the film would undergo the transition. The transition could be cycled with no change in the transmission properties or the width of the hysteresis.

![Graph showing infrared switching at 2.5 μm and hysteresis curves for VO₂ films doped with 0.3, 0.6, and 1.2 atom% W prepared from the APCVD reaction of VCl₄, H₂O and [W(OCH₃)₃].](image)

There was a linear relationship between the change in thermochemical transition temperature and the amount of tungsten doped into the vanadium(IV) oxide thin films as shown in Figure 44. There was an approximately 21 °C decrease in thermochemical transition temperature for every 1 atom% tungsten doped into the vanadium(IV) oxide thin films prepared by the APCVD reaction of vanadium(IV) chloride, water and tungsten(VI) ethoxide. This was in agreement with results reported for tungsten doped vanadium(IV) oxide prepared by PVD methods.
To give an indication of the effectiveness of the tungsten doped vanadium(IV) oxide thin films as intelligent window coatings the transmittance and reflectance spectra of the films were measured below and above the metal-to-semiconductor transition, an example of which is shown in Figure 45. The transmittance of the films below the transition temperature showed a maximum at about 600 nm, in the orange-yellow region, the films also showed a high transmittance in the near infrared region below the thermochromic transition temperature. The reflectance spectra of a tungsten doped film below the thermochromic transition temperature showed a minimum at about 500 nm, in the blue-green region, with a general slight increase in reflectivity with wavelength. When the temperature of the films was increased there was no appreciable change in the transmittance or reflectance in the visible region but a dramatic change in the near infrared region was observed. The transmittance decreased significantly by 20-25 % across the near infrared range measured and the reflectance increased by 10-15 % at wavelengths greater than 1800 nm.
3. APCVD of tungsten doped vanadium(IV) oxide

![Reflectance and transmittance spectra](image)

Figure 45. Reflectance and transmittance spectra below and above the thermochromic transition temperature for a 0.6 atom% W doped VO₂ thin film prepared from the APCVD reaction of VCl₄, H₂O and [WOC₂H₅₂] at 600 °C.

3.3.2.1 Film preparation and characterisation.

In section 2.3.1.2 it was described how thin films of vanadium(IV) oxide could be deposited onto glass substrates by the APCVD reaction of vanadium(V) oxytrichloride and water at temperatures above 600 °C with a slight excess of water over vanadium(V) oxytrichloride. As with the vanadium(IV) chloride and water system, the introduction of tungsten as a dopant should reduce the metal-to-semiconductor transition temperature to closer to room temperature. By using the conditions developed for the APCVD of vanadium(IV) oxide from vanadium(V) oxytrichloride and water, tungsten doped vanadium oxides were prepared using tungsten(VI) chloride as the tungsten source.

An attempt was made to deposit tungsten oxide films from the APCVD reaction of tungsten(VI) chloride and water at the conditions necessary for the deposition of vanadium(IV) oxide. These experiments gave particulate deposits on the substrate that were yellow in colour. There was insufficient material for X-ray diffraction.

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3. APCVD of tungsten doped vanadium(V) oxide

analysis but Raman spectroscopy gave the spectrum shown in Figure 46, which showed bands at 144, 201, 270, 316, 371, 427, 651, 700, 805, 956 and 980 cm\(^{-1}\). The strongest bands at 207, 700, and 805 cm\(^{-1}\) corresponded to Raman bands of monoclinic WO\(_3\)\(^{\text{m}}\) as described in section 3.3.1.1. The remaining bands, labelled in red in Figure 46, corresponded to Raman bands of vanadium(V) oxide resulting from residual vanadium(V) oxytrichloride in the CVD apparatus. This confirms that tungsten(VI) oxide could be used as a precursor for the CVD of tungsten oxide films and has led to further successful work in the Parkin group.\(^{101}\)

![Figure 46. Raman spectrum of particulate film produced from the APCVD reaction of WCl\(_6\) and H\(_2\)O at 650 °C. Bands marked in red indicate V\(_2\)O\(_5\) bands resulting from residual VOCl\(_3\) in apparatus.](image)

Thin films of tungsten doped vanadium oxide were prepared by the APCVD reaction of vanadium(V) oxytrichloride, water and tungsten(VI) chloride, these films were visually similar to undoped vanadium(IV) oxide films deposited from vanadium(V) oxytrichloride and water. The introduction of tungsten(VI) oxide into the APCVD system appeared to reduce the amount of mixed phase V\(_2\)O\(_{15}\)-V\(_3\)O\(_5\) at the leading edge of the substrate, in many cases this type of deposit did not occur. The films were characterised by Raman spectroscopy and X-ray diffraction. X-ray photoelectron spectroscopy was used to determine the phase and composition of the vanadium oxide films deposited. The thermochromic phase transition was
examined by Raman spectroscopy, X-ray diffraction and visible/IR reflectance and transmittance. The results of these analyses are summarised in Table 4.

<table>
<thead>
<tr>
<th>Reactor temp. / °C</th>
<th>Gas phase amount of WCl₆ / mol min⁻¹</th>
<th>Gas phase amount of VOCl₃ / mol min⁻¹</th>
<th>Gas phase amount of H₂O / mol min⁻¹</th>
<th>Phase from Raman and XRD</th>
<th>W atom% in film</th>
<th>Transition temperature ± hysteresis width / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>0.002</td>
<td>0.014</td>
<td>0.026</td>
<td>VO₃(M)</td>
<td>0.6</td>
<td>43 ± 6</td>
</tr>
<tr>
<td>650</td>
<td>0.004</td>
<td>0.026</td>
<td>0.026</td>
<td>VO₃(M)</td>
<td>0.3</td>
<td>55 ± 7</td>
</tr>
<tr>
<td>650</td>
<td>0.008</td>
<td>0.024</td>
<td>0.026</td>
<td>VO₃(M)</td>
<td>1.2</td>
<td>35 ± 3</td>
</tr>
<tr>
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<td>0.010</td>
<td>0.019</td>
<td>0.026</td>
<td>VO₃(R)</td>
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<td>10 (2)</td>
</tr>
<tr>
<td>650</td>
<td>0.001</td>
<td>0.021</td>
<td>0.026</td>
<td>VO₃(M)</td>
<td>0.4</td>
<td>55 ± 6</td>
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<td>0.010</td>
<td>0.015</td>
<td>0.026</td>
<td>VO₃(R)</td>
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<td>5 (2)</td>
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<td>650</td>
<td>0.006</td>
<td>0.017</td>
<td>0.026</td>
<td>VO₃(M)</td>
<td>0.9</td>
<td>41 ± 3</td>
</tr>
<tr>
<td>650</td>
<td>0.008</td>
<td>0.021</td>
<td>0.026</td>
<td>VO₃(M)</td>
<td>0.7</td>
<td>45 ± 6</td>
</tr>
<tr>
<td>650</td>
<td>0.009</td>
<td>0.020</td>
<td>0.026</td>
<td>VO₃(M)</td>
<td>1.9</td>
<td>29 (2)</td>
</tr>
</tbody>
</table>

Table 4. Conditions used to prepare tungsten doped VO₂ thin films from the APCVD reaction of VOCl₃, H₂O and WCl₆. *Hysteresis width only measurable with Tc above 30 °C.

Figure 47. The curved relationship between amount of gas phase WCl₆ to atom% W in VO₂ thin films prepared from VOCl₃ and water. The line is added as a guide to the eye.
In all cases vanadium(IV) oxide was obtained, the amount of tungsten found in the films could be related to the amount of tungsten(VI) chloride precursor in the gas phase; the highest amount of gas phase tungsten(VI) chloride gave the greatest atom% of tungsten in the vanadium oxide thin films. A curved relationship between the amount of gas phase tungsten(VI) chloride and atom% tungsten in the film was obtained as shown in Figure 47. At low flow-rates the tungsten(VI) chloride bubbler was prone to blockages and this probably accounts for the curved relationship between gas phase amount of tungsten(VI) chloride and the amount of tungsten in the films.

Figure 48. XRD pattern of a 0.7 atom% W doped VO_2 thin film prepared by the APCVD reaction of VOCl_3, H_2O and WCl_6 at 650 °C. Also shown is a literature match pattern for VO_2(M).

X-ray diffraction of the tungsten doped vanadium(IV) oxide thin films prepared from vanadium(V) oxytrichloride, water and tungsten(VI) chloride films showed reflections at 27.8 ° and 57.5 ° (Figure 48) corresponding to the (011) and (022) planes of the monoclinic phase of vanadium(IV) oxide respectively. This strongly indicated that the films were preferentially orientated along the (011) plane. Insufficient reflections were observed for accurate cell parameters to be calculated.
3. APCVD of tungsten doped vanadium(IV) oxide

and Miller indices were assigned by comparison to literature patterns. The films containing sufficient tungsten so that the metal-to-semiconductor phase transition occurred below room temperature showed reflections at 27.7 ° and 55.4 °. These reflections corresponded to the (110) and (211) planes of the tetragonal phase of vanadium(IV) oxide respectively as shown in Figure 49.

![XRD pattern of 2.6 atom% W doped VO₂](image)

Figure 49. XRD pattern of 2.6 atom% W doped VO₂ prepared from the APCVD reaction of VOCl₃, H₂O and WCl₆ at 650 °C. Also shown is a match pattern for VO₂(R).

The morphology of the tungsten doped vanadium(IV) oxide films prepared from vanadium(V) oxytrichloride, water and tungsten(VI) chloride was significantly different to that of the undoped vanadium(IV) oxide thin films prepared from vanadium(V) oxytrichloride and water. Scanning electron microscopy (Figure 50 and Figure 51) showed thin worm-like structures, with a width of about 10 nm and a length varying between 100 and 800 nm, almost perpendicular to the substrate. The morphology of the films may explain the preferred orientation observed in the X-ray diffraction patterns of the tungsten doped vanadium(IV) oxide thin films. This is unusual growth morphology and is an extreme form of the Volmer-Weber island growth mechanism.
3. APCVD of tungsten doped vanadium(IV) oxide

X-ray photoelectron spectroscopy was used to determine the composition of the tungsten doped vanadium(IV) oxide thin films prepared from vanadium(V)
oxytrichloride, water and tungsten(VI) chloride. Wide range survey spectra of the surface of the films showed XPS peaks for oxygen, vanadium, tungsten, silicon, carbon and nitrogen. No chlorine was detected in any of the tungsten doped vanadium(IV) oxide thin films. As described for previous XPS studies in sections 2.3.1.3 and 3.3.1.1, nitrogen was an atmospheric contaminant and carbon could be attributed to atmospheric carbon dioxide and to hydrocarbons from the oil diffusion pump of the vacuum chamber. Both surface contaminants were easily removed by argon ion etching. The peaks due to silicon were from the glass substrate that was exposed through pinhole defects in the deposited vanadium oxide films. Quantitative analysis was performed on the first etched layer of the film using the O1s, V2p and W4f XPS peaks. Oxidation state analysis was performed on the O1s, V2p and W4f XPS peaks of the surface layer to avoid possible problems with changes in valence caused by argon ion etching. These peaks were chosen because literature assignments were more readily available. Compositional analysis obtained from the XPS data is given in Table 4. The lowest amount of tungsten introduced into the vanadium(IV) oxide lattice was 0.3 atom% and the highest was 3.1 atom%. Tungsten was found to be homogeneously distributed throughout the vanadium oxide films as indicated by depth profiling analysis.

High-resolution analysis of the O1s and V2p XPS peaks (Figure 52) indicated that the vanadium was present in two forms, \( V^{4+} \) with a binding energy of 515.8 eV and \( V^{5+} \) with a binding energy of 513.6 eV. The O1s peak could be deconvoluted to two components relating to oxygen bound to a transition metal with a binding energy of 530.4 eV, and oxygen bound to silicon from the glass substrate with a binding energy of 532.1 eV.

Deconvolution of the W4f peaks indicated that the tungsten was present as \( W^{4+} \), with \( W4f_{7/2} \) and \( W4f_{5/2} \) binding energies of 34.5 and 32.6 eV respectively. As with the tungsten doped thin films prepared from vanadium(IV) chloride, water and tungsten(VI) ethoxide, the tungsten had undergone a reduction when incorporated into the vanadium(IV) oxide lattice. If the reduction of tungsten was caused by it's incorporation into the vanadium(IV) oxide lattice the presence of \( V^{5+} \) due to charge compensation would be expected, so the reduction of the tungsten ions must have occurred before film formation. If tungsten(III) species were formed prior to the
incorporation of tungsten into the vanadium oxide film (tungsten(III) chloride species are known\textsuperscript{1,5}), then the formation of $V^{3+}$ is easily explained. The reduction of one $V^{4+}$ cation by each $W^{3+}$ species could form the detected $W^{2+}$ and $V^{3+}$ cations. Alternatively, tungsten(IV) species could be formed during gas phase or surface reactions and then migrate to a nucleation site. This would not explain the presence of $V^{3+}$ in the thin film.

![Figure 52. Deconvoluted O1s and V2p XPS peaks of a 2.6 atom\% W doped VO\textsubscript{2} thin film prepared from the APCVD reaction of VOCl\textsubscript{3}, H\textsubscript{2}O, and WCl\textsubscript{4} at 650 °C.](image)

The formation of reduced vanadium ions in tungsten doped vanadium(IV) oxide thin films helps to explain the observed thermochromic transition temperatures of the films. The low temperature semiconducting phase would be destabilised by the presence of the $V^{3+}$ and thus reduce the thermochromic transition temperature. These observations are complementary to the theory Tang \textit{et al.}\textsuperscript{3} described in section 1.5, who suggested that the formation of $V^{3+}$ on tungsten doping causes a
destabilisation of the monoclinic phase of vanadium(IV) oxide and reduces the metal-to-semiconductor transition temperature.

![Deconvoluted V3p, W4f and O2p XPS peaks for a 2.6 atom% W doped VOx thin film prepared from the APCVD reaction of VOCl3, H2O, and WCl6 at 650 °C.](image)

### 3.3.2.2 THERMOCHROMIC PROPERTIES.

The thermochromic properties of the tungsten doped vanadium(IV) oxide thin films prepared from vanadium(V) oxytrichloride, water and tungsten(VI) chloride were examined by X-ray diffraction, Raman spectroscopy and visible/IR reflectance-transmittance spectroscopy. The thermochromic transition temperatures of the thin films were measured by their infrared transmittance with varying temperature.
The X-ray diffraction at different temperatures of a 0.7 atom% tungsten doped vanadium(IV) oxide thin film was performed to reveal the monoclinic (011) reflection transforming into the tetragonal (110) reflection when the temperature was increased (Figure 54). As with similar studies on thin films of tungsten doped vanadium(IV) oxide prepared from the APCVD reaction of vanadium(IV) chloride, water and tungsten(VI) ethoxide the first order transition was clearly observed with both phases of vanadium(IV) oxide present as the metal-to-semiconductor transition occurred. The reversibility of the transition was also displayed with the monoclinic (011) reflection returning when the sample was cooled back to room temperature. The transition temperature for the 0.7 atom% tungsten doped vanadium(IV) oxide thin film was taken to be 55 °C, where the monoclinic and tetragonal reflections were of equal intensity.
When the tungsten content of a vanadium(IV) oxide thin film was above 2 atom% the transition temperature was below 25 °C. The Raman spectra at temperatures down to −15 °C, for a 3.1 atom% tungsten doped vanadium(IV) oxide thin film deposited from vanadium(V) oxytrichloride, water and tungsten(VI) chloride is shown in Figure 55. There were no Raman bands apparent at 30 °C, the broad feature at 555 cm$^{-1}$ usually observed in the Raman spectrum of the high temperature phase of vanadium(IV) oxide was not seen. On cooling to 5 °C a very weak band at 221 cm$^{-1}$ was seen, as was the broad feature at 555 cm$^{-1}$, indicating the film was at the transition point. By cooling further to −5 °C more Raman bands for the monoclinic phase of vanadium(IV) oxide were observed, bands at 195, 222 and 610 cm$^{-1}$ were present in the spectrum. At −15 °C an almost complete set of Raman bands for monoclinic vanadium(IV) oxide were observed, with peaks at 195, 222, 307, 500 and 610 cm$^{-1}$. When the film was heated back up to room temperature no Raman bands were observed in the spectrum indicating that the material had returned to the high temperature, metallic phase of vanadium(IV) oxide. This was an important result showing the ability of the vanadium(V) oxytrichloride, water
and tungsten(VI) chloride APCVD system to prepare tungsten doped vanadium(IV) oxide with tungsten contents high enough to give thermochromic switching temperatures well below room temperature.

![Graph showing infrared switching properties](image)

The infrared switching properties of tungsten doped vanadium(IV) oxide thin films with tungsten contents between 0.4 and 1.2 atom% are shown in Figure 56. As the tungsten content was increased, the transition occurred at a reduced temperature. The hysteresis width of the transition was quite broad for the 0.4 and 0.8 atom% tungsten containing films but narrowed considerably for the 1.2 atom% film, however the sharpness of the transition for the 1.2 atom% tungsten film was significantly reduced. The transmittance of the low temperature, semiconducting phase of the films reduced with increasing tungsten content. This was in accordance with results described in section 3.3.1.2, with the transmittance of the high temperature, metallic phase increasing slightly as the tungsten content of the films was increased. As such the optical contrast between the two phases was reduced as the tungsten content of the thin films was increased. For a 0.4 atom% tungsten
doped vanadium(IV) oxide thin film the optical contrast between the semiconducting and metallic phases was about 50%. This was reduced to about 30% for a 1.2 atom% tungsten doped vanadium(IV) oxide thin film. Infrared hysteresis curves for vanadium(IV) oxide thin films with higher tungsten contents could not be measured by this method as it was not possible to cool the heating cell below room temperature in a controlled manner. Thermochromic transition temperatures for thin films containing higher tungsten contents were obtained by Raman spectroscopy.

![Graph](image)

**Figure 5.7. Relationship between W content of doped VO₂ thin films and thermochromic transition temperature.**

When the transition temperature was plotted against the tungsten content of the doped vanadium(IV) oxide thin films a linear relationship was observed as shown in Figure 5.7. This agreed with the tungsten doped vanadium(IV) oxide thin films described in section 3.3.1.2. The reduction in transition temperature was approximately 19 °C for each 1 atom% tungsten doped into the vanadium(IV) oxide lattice and was in agreement with the results reported in section 3.3.1 and for tungsten doped vanadium(IV) oxide thin films prepared by PVD methods.\(^{10,34}\)

The reflectance-transmittance spectra of a 0.6 atom% tungsten doped vanadium(IV) oxide thin films is shown in Figure 5.8. The change in transmittance
3. APCVD of tungsten doped vanadium(IV) oxide

properties was quite dramatic in the infrared region, with no appreciable change in the visual transmittance, when the temperature of the thin film was increased from room temperature to a temperature above which the metal-to-semiconductor transition occurred. There was an equally dramatic change in reflectance properties between the two states, at low temperature the reflectance spectrum was fairly constant over the wavelength range measured, but when the temperature was increased to above the transition temperature of the material, the reflectance of the material increased significantly, especially in the infrared region but also in the visible region. This is exactly the response required if the APCVD prepared tungsten doped vanadium(IV) oxide thin films are to find use as intelligent window coatings.

![Figure 58. Reflectance-transmittance spectra for a 0.6 atom% W doped VO$_2$ thin film below and above the thermochromic transition temperature. Discontinuities are due to lamp and filter changes in instrument.](image)

3.4 Conclusions and further discussion.
Two precursor systems were successfully used to prepare thin films of tungsten doped vanadium(IV) oxide. Firstly, tungsten(VI) ethoxide was introduced into the vanadium(IV) chloride and water system described in section 2.3.1.1. This gave vanadium(IV) oxide thin films containing between 0.3 and 1.2 atom% tungsten and
with thermochromic transition temperatures of 58 °C for a 0.3 atom% tungsten doped film to as low as 42 °C for a 1.2 atom% tungsten doped vanadium(IV) oxide thin film.

Tungsten(VI) ethoxide was not considered to be an ideal precursor for doping tungsten into vanadium(IV) oxide thin films as its low vapour pressure and transport properties prevented tungsten contents of much greater than 1.2 atom% from being introduced into the vanadium(IV) oxide lattice.

The thermochromic properties of these films did show promise as intelligent window coatings with transition temperatures approaching room temperature and the typical change in optical properties associated with undoped vanadium(IV) oxide. Raman spectroscopy and X-ray diffraction indicated that the tungsten formed a solid solution with the vanadium(IV) oxide and did not form a separate phase of tungsten oxide.

X-ray photoelectron spectroscopy revealed that the tungsten was introduced into the vanadium(IV) oxide as tungsten(IV) cations, suggesting a reduction of the tungsten occurred during the CVD process. Also no carbon from the ethoxide fragments was integrated into the tungsten doped vanadium(IV) oxide films which would have degraded the thermochromic properties of the thin films.

The second tungsten precursor investigated was tungsten(VI) chloride, which was introduced into the vanadium(V) oxytrichloride and water system described in section 2.3.1.2. This system was much more successful than the tungsten(VI) ethoxide system, as the higher vapour pressure and transport properties of tungsten(VI) chloride enabled a greater amount of tungsten to be introduced into the vanadium(IV) oxide lattice. Tungsten contents as high as 3 atom% were observed which gave thermochromic transition temperatures as low as 5 °C. A tungsten content of 1.9 atom% gave a thermochromic transition temperature of 29 °C, which is around the ideal for intelligent window coatings.

Raman spectroscopy and X-ray diffraction indicated that there was no phase segregation of the tungsten oxide in any of the films and the tungsten formed a solid solution with the vanadium(IV) oxide. X-ray photoelectron spectroscopy revealed that the tungsten had an oxidation state of +4 in the vanadium(IV) oxide.
3. APCVD of tungsten doped vanadium(IV) oxide

thin films, suggesting a reduction from the tungsten(VI) chloride precursor during the CVD process.

The tungsten doped vanadium(IV) oxide thin films from both precursor systems displayed decreasing luminous transmittance in the low temperature, semiconducting phase with increasing tungsten content, which would be disadvantageous in commercial glazing applications. These detrimental effects to the infrared switching characteristics are common to doped vanadium(IV) oxide thin films. Lithium doping has been shown to have the largest adverse effect on the infrared transmittance of the low temperature, monoclinic phase of vanadium(IV) oxide, with a 1 atom% lithium doped vanadium(IV) oxide thin film of 380 nm thickness showing only a 5% transmittance of 2.0 μm radiation.

As discussed in section 1.2 the luminous transmittance of vanadium(IV) oxide can be increased without adversely affecting the material’s thermochromic properties by applying an overlayer of an antireflective material such as silicon(IV) oxide or titanium(IV) oxide. The addition of an overlayer would also be possibly advantageous in increasing the mechanical stability of the vanadium(IV) oxide thin films prepared by APCVD. Titanium(IV) oxide would also make the coating multifunctional due to the well characterised photocatalytic properties of the material.

The hysteresis width of the thermochromic transition increased with increasing tungsten content of the doped vanadium(IV) oxide thin films. This is a common result in doped thin films of vanadium(IV) oxide and is probably related to an increase in the number of defects and the small particle size of the thin films. Tungsten is not the only dopant to affect the metal-to-semiconductor transition temperature of vanadium(IV) oxide and doping other transition metal ions into the vanadium(IV) oxide lattice will be the focus of chapter 4.
Chapter 4

ATMOSPHERIC PRESSURE CHEMICAL VAPOUR DEPOSITION OF METAL DOPED VANADIUM(IV) OXIDE.

4.1 Introduction.
In Chapter 3 the atmospheric pressure chemical vapour deposition of tungsten doped vanadium(IV) oxide was described. Tungsten doping is known to reduce the thermochemical transition temperature of vanadium(IV) oxide by the greatest amount on a per atom% basis. Other metal ions also have a profound effect on the metal-to-semiconductor transition temperature of vanadium(IV) oxide and so an attempt was made to dope a selection of other metal ions into the vanadium(IV) oxide lattice by the APCVD method described in previous chapters. This chapter will describe the attempts made to dope chromium, molybdenum, niobium, titanium and tin ions into vanadium(IV) oxide thin films using the APCVD reactions developed in chapter 2.

Chromium and molybdenum are in the same group as tungsten and both show a wide range of oxidation states, which may be an important factor in disrupting the V\textsuperscript{IV}-V\textsuperscript{IV} homopolar bonds of the low temperature, monoclinic phase of vanadium(IV) oxide as observed for tungsten doping. For chromium doping chromium(VI) oxychloride is potentially an ideal precursor. It is a very volatile, reactive liquid that can be used to prepare chromium oxide thin films by CVD. Chromium(III) ions have been doped into the vanadium(IV) oxide lattice by sol-gel methods where it was shown to increase the thermochemical transition temperature of the material. Molybdenum(V) chloride is a volatile solid that has been used to prepare molybdenum phosphide thin films by an APCVD method and as such may be suitable for the deposition of molybdenum oxide thin films and to dope molybdenum into the vanadium(IV) oxide lattice by APCVD. Molybdenum doping of vanadium(IV) oxide thin films has been successfully
achieved by PVD\textsuperscript{44,45} and sol-gel\textsuperscript{41} methods. In both cases a reduction in the thermochromic transition temperature was observed, with a molybdenum content of 7 atom\% resulting in a thermochromic transition temperature of 24 °C.\textsuperscript{41}

Niobium is a member of the same group as vanadium. Niobium(IV) oxide has been shown to exhibit a metal-to-semiconductor transition at 800 °C,\textsuperscript{28} while niobium(II) oxide shows metallic conductivity at room temperature.\textsuperscript{85} Niobium ions have been successfully doped into the vanadium(IV) oxide lattice by sol-gel\textsuperscript{36,42,104} methods but surprisingly niobium doping into vanadium(IV) oxide thin films by PVD methods has not been reported. Niobium doping has a similar effect to molybdenum on the metal-to-semiconductor transition of vanadium(IV) oxide, 7 atom\% niobium can reduce the transition temperature to —4 °C.\textsuperscript{7} Niobium(V) chloride has a relatively high vapour pressure\textsuperscript{105} and has recently been reported as a precursor for the APCVD of niobium(V) oxide thin films on glass substrates.\textsuperscript{106} It would therefore appear to be a suitable precursor for doping niobium into the vanadium(IV) oxide lattice.

Titanium is the last transition metal to be investigated as a dopant for vanadium(IV) oxide in this thesis. Titanium(II) oxide shows metallic conductivity over a broad range of temperatures\textsuperscript{18} and titanium(IV) oxide is a well characterised photocatalytic material\textsuperscript{14} which may give the vanadium(IV) oxide thin films some multifunctional properties. Titanium ions have been successfully doped into vanadium(IV) oxide thin films by sol-gel methods,\textsuperscript{36,38} and the thin films indicated an increase in the thermochromic transition temperature from the undoped material. Titanium(IV) chloride is a reactive, volatile liquid\textsuperscript{48} which has been extensively used to prepare titanium(IV) oxide thin films by CVD\textsuperscript{15} and should be ideal for doping titanium ions into vanadium(IV) oxide thin films.

The final dopant for vanadium(IV) oxide to be investigated here was tin. Tin is a main group metal forming a stable dioxide with the rutile structure\textsuperscript{84,85} and so may be easily doped into the related monoclinic vanadium(IV) oxide lattice. Tin(IV) also has a much larger covalent radius (1.40 Å) than the ionic radius of vanadium(IV) (0.58 Å).\textsuperscript{67} This may cause a large depression in the thermochromic phase transition if an accompanying oxidation-reduction of tin and vanadium can occur, as appears to happen when tungsten is introduced into the vanadium(IV) oxide lattice. Tin
doping into vanadium(IV) oxide thin films has been achieved by a PVD method which showed an increase in the thermochromic transition temperature and a reduction in optical contrast between the low temperature and high temperature phases with increasing tin content. Tin(IV) chloride is a volatile, reactive liquid which has been used to form tin oxide thin films by an APCVD reaction and so should be highly suitable for doping tin into vanadium(IV) oxide thin films by APCVD.

4.2 Experimental.
All APCVD reactions were performed on the apparatus described in section 2.2. A dopant precursor was transferred to bubbler 1 and introduced into the CVD reactor at the same time as the vanadium precursor and water. This procedure was repeated for each dopant precursor. Film characterisation consisted of the analyses performed for the vanadium oxide thin films prepared in chapters 2 and 3.

4.3 Results and discussion.
4.3.1 APCVD of VOCl₃, H₂O and CrO₂Cl₂
4.3.1.1 Film preparation and characterisation.
Using the conditions determined in section 2.3.1.2 to produce vanadium(IV) oxide from the APCVD reaction of vanadium(V) oxytrichloride and water, the chromium doping of vanadium(IV) oxide was attempted by introducing chromium(VI) oxychloride into the CVD system. The conditions used to prepare the chromium containing vanadium oxide thin films are given in Table 5.

All of the chromium containing vanadium oxide thin films were dark yellow in colour and covered the entire substrate evenly. The films were fairly adherent, passing the Scotch tape test and were not easily removed by rubbing with a tissue. The films could be scratched with a brass stylus and a steel scalpel. The XRD and Raman patterns did not match any database patterns and may indicate a new phase of chromium vanadium oxide. The XRD patterns (Figure 59) showed reflections at 13.7°, 27.2°, 27.7°, 33.3°, 34.0°, 34.9°, 40.6°, 41.3°, and 42.1°. The XRD patterns of the chromium vanadium oxide thin films was indexed, using the Treor algorithm, to a triclinic unit cell with dimensions $a = 3.4292 \text{ Å}$, $b =$
4. APCVD of metal doped vanadium(IV) oxide

5.3233 Å and \( t = 8.0409 \) Å, and unit cell angles \( \alpha = 56.796^\circ, \beta = 69.953^\circ \) and \( \gamma = 78.245^\circ \). The Miller indices of the reflections for this cell are shown in Figure 59. The reflections labelled * in Figure 59, were unassigned in the Treor analysis.

<table>
<thead>
<tr>
<th>Reactor temperature / °C</th>
<th>Gas phase amount CrO(_2)Cl(_2) / mol min(^{-1})</th>
<th>Gas phase amount VOCl(_3) / mol min(^{-1})</th>
<th>Gas phase amount H(_2)O / mol min(^{-1})</th>
<th>Cr:V:O ratio in thin film by XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>0.0002</td>
<td>0.040</td>
<td>0.026</td>
<td>4:3:3</td>
</tr>
<tr>
<td>650</td>
<td>0.0006</td>
<td>0.048</td>
<td>0.026</td>
<td>4.5:2.63</td>
</tr>
<tr>
<td>650</td>
<td>0.0010</td>
<td>0.085</td>
<td>0.026</td>
<td>1:6:3</td>
</tr>
<tr>
<td>650</td>
<td>0.0011*</td>
<td>0.032</td>
<td>0.026</td>
<td>5:2:3</td>
</tr>
<tr>
<td>650</td>
<td>0.0023</td>
<td>0.040</td>
<td>0.026</td>
<td>3:1:3</td>
</tr>
</tbody>
</table>

Table 5. Conditions used to prepare chromium vanadium oxide thin films from the APCVD reaction of VOCl\(_3\), H\(_2\)O and CrO\(_2\)Cl\(_2\).

Figure 59. XRD pattern for a chromium vanadium oxide thin film prepared from the APCVD reaction of VOCl\(_3\), H\(_2\)O and CrO\(_2\)Cl\(_2\) at 650 °C.

Reflections marked * were unassigned in Treor indexing.

All of the chromium vanadium oxide thin films gave similar Raman spectra, an example of which is shown in Figure 60. Raman bands were observed at 200, 221,
4. APCVD of metal doped vanadium(V) oxide

252, 297, 346, 400, 427, 477, 496, 534, 665, 772, 826, 886, 923, and 985 cm$^{-1}$. The weak band at 1325 cm$^{-1}$ (marked * in Figure 60) was an emission line from the room lights.

Comparison of the Raman spectrum of chromium vanadium oxide thin films with literature spectra of Cr$_2$O$_6$\textsuperscript{109}, Cr$_7$O$_8$\textsuperscript{110} and Cr$_3$O$_5$\textsuperscript{111} revealed some similarities. The general appearance and band positions of the chromium vanadium oxide thin films were very similar to those of Cr$_2$O$_6$ and Cr$_3$O$_5$, especially the bands at 886 and 923 cm$^{-1}$ of the chromium vanadium oxide thin films. These appeared in the region assigned to terminal Cr$^{5+}$-O stretching modes of chromate species in Cr$_2$O$_6$ and Cr$_3$O$_5$. It is reported that mixed valence chromium compounds XCr$_6$O$_8$ (X = Na, K, Rb) share structural resemblances with Cr$_2$O$_6$ and Cr$_3$O$_5$ and that the Raman spectra of these compounds were qualitatively similar.\textsuperscript{111} The X-ray diffraction patterns of the XCr$_6$O$_8$ compounds also showed some similarities with the chromium vanadium oxide thin films,\textsuperscript{111} which may indicate a possible relation in the structure of the chromium vanadium oxide thin films and XCr$_6$O$_8$ compounds. The structure of the XCr$_6$O$_8$ compounds could be described as being formed from layers of corner sharing Cr$^{5+}$O$_6$ octahedra and Cr$^{3+}$O$_4$ tetrahedra with a monoclinic unit cell.\textsuperscript{111}

![Figure 60. Raman spectrum for a chromium vanadium oxide thin film prepared by the APCVD reaction of VOCl$_3$, H$_2$O and CrO$_2$Cl$_2$ at 650 °C. * = emission line from room lighting.](image-url)
4. APCVD of metal doped vanadium(IV) oxide

The XRD patterns and Raman spectra did not appear to be affected by the relative amount of chromium and vanadium in the thin films, suggesting that all the compositions had a similar structure. X-ray photoelectron spectroscopy was used to determine the elemental composition of the chromium vanadium oxide thin films and these are shown in Table 5. The compositions were such that chromium was present in quantities much greater than could be considered as doping amounts, and in most cases were present in excess of vanadium, reinforcing the supposition that a compound of chromium vanadium oxide was formed.

![Figure 61. Cr2p XPS peaks, showing deconvoluted Cr2p\(3/2\) peak, for a chromium vanadium oxide thin film prepared from the APCVD reaction of VOCI\(_3\), H\(_2\)O and CrO\(_2\)Cl\(_2\) at 650°C.](image)

As with XPS studies in previous sections, broad range survey spectra revealed that the surface of the thin film was contaminated with carbon and nitrogen, which were removed by argon ion etching. Silicon could also be detected through pinhole defects in the thin films exposing the substrate to the incident X-rays. Deconvolution of the Cr2p\(3/2\) XPS signal, for which most reference data was available,\(^6\) gave a single peak (Figure 61) with a binding energy of 576.7 eV, which
could be assigned to either Cr\textsuperscript{3+} or Cr\textsuperscript{4+}. As the most stable oxidation state for chromium is the +3 state,\textsuperscript{48} the Cr\textsuperscript{3+} state seems the most likely assignment. The binding energy for the Cr2p\textsubscript{3/2} electron as Cr\textsuperscript{6+} is 580 eV,\textsuperscript{38} much higher than that measured in these chromium vanadium oxide thin films and was obviously not present in these films.

Deconvolution of the V2p\textsubscript{3/2} and O1s XPS peaks for the chromium vanadium oxide thin films (Figure 62) gave a single vanadium peak with a binding energy of 516.0 eV, corresponding to V\textsuperscript{4+}, and two O1s peaks with binding energies of 532.2 eV, corresponding to oxygen bound to silicon, and 530.7 eV, corresponding to oxygen bound to chromium or vanadium.

![Graph](image-url)

**Figure 62** O1s and V2p XPS peaks, showing deconvoluted O1s and V2p\textsubscript{3/2} peaks, for a chromium vanadium oxide thin film prepared from the APCVD reaction of VOCl\textsubscript{3}, H\textsubscript{2}O and CrO\textsubscript{2}Cl\textsubscript{2} at 650 °C.

The oxidation state analysis indicates that the chromium ions must undergo a reduction from the chromium\textsuperscript{(VI)} ions of the CrO\textsubscript{2}Cl\textsubscript{2} precursor during the film deposition process. Chromium\textsuperscript{(VI)} is highly oxidising, and as the vanadium ions in
4. APCVD of metal doped vanadium(IV) oxide

The thin film were also in a reduced state compared to the VOCl₃ precursor, it was assumed that the chromium was reduced before film formation occurred. This could happen either in the gas phase or as an adsorbed species prior to migration to a nucleating site. A Cr⁶⁺ species at the nucleating site would probably oxidise vanadium ions to the +5 state. Scanning electron microscopy of the chromium vanadium oxide thin films showed a particulate morphology with particle sizes in the range 30 to 100 nm. These particles formed island aggregates that merged to form the thin film. This type of growth morphology is consistent with a thin film rapidly grown on a highly nucleating substrate. The chromium vanadium oxide thin films did show some hydrophilic properties, a 1 µL drop of water had a contact angle of 53.7° after exposing the film to UV radiation for 1 hour, dropping from a contact angle of 87.3° prior to irradiation. The particulate nature of the films and their apparently high surface area probably contributed to this phenomenon.

Figure 63. SEM of a chromium vanadium oxide thin film prepared from the APCVD reaction of VOCl₃, H₂O and CrO₂Cl₂ at 650 °C.
4. APCVD of metal doped vanadium(V) oxide

4.3.1.2 Thermochromic properties.

None of the chromium vanadium oxide thin films displayed any thermochromic behaviour over the temperature range investigated (<80 °C). The thin films of chromium vanadium oxide did not show any of the properties required for use as intelligent window coatings. The room temperature reflectance-transmittance spectra for a chromium vanadium oxide thin film are shown in Figure 64. The films showed a high transmittance in the infrared region of the spectrum but were quite opaque in the visible region. The reflectance was fairly low for all wavelengths with a small peak at about 1130 nm. These spectra indicated that the thin films of chromium vanadium oxide were not suitable for use in solar control applications, which require a high infrared reflectance and a high visible transmittance.

![Figure 64. Room temperature reflectance-transmittance spectra for a chromium vanadium oxide thin films prepared from the APCVD reaction of VOCl₃, H₂O and CrO₂Cl₂ at 650 °C.](image)

Despite the lack of thermochromic properties for the chromium vanadium oxide thin films they may have other technological applications. If they have a layered structure similar to Cr₂O₃ and Cr₃O₅ then there may be scope for their use as electrode materials in solid-state batteries as with the chromium oxides."
4. APCVD of metal doped vanadium(IV) oxide

4.3.2 APCVD of VOCl₃, H₂O and MoCl₅

4.3.2.1 Film preparation and characterisation.

Molybdenum containing vanadium oxide thin films were prepared from the APCVD reaction of vanadium(V) oxytrichloride, water and molybdenum(V) chloride using the conditions described in section 2.3.1.2 to give vanadium(IV) oxide. The conditions used to prepare molybdenum doped vanadium(IV) oxide thin films are given in Table 6.

<table>
<thead>
<tr>
<th>Reactor temperature / °C</th>
<th>Gas phase amount MoCl₅ / mol min⁻¹</th>
<th>Gas phase amount VOCl₃ / mol min⁻¹</th>
<th>Phase of film from Raman and XRD</th>
<th>%Mo in film by XPS</th>
<th>Tₑ / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>0.0003</td>
<td>0.053</td>
<td>VO₂(M)</td>
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<td>48 ± 5</td>
</tr>
<tr>
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<td>0.040</td>
<td>VO₂(M)</td>
<td>0.3</td>
<td>47 ± 3</td>
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<tr>
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<td>VO₂(M)</td>
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<tr>
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<tr>
<td>650</td>
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<td>0.044</td>
<td>VO₂(M)</td>
<td>0.02</td>
<td>58 ± 10</td>
</tr>
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</table>

Table 6. Conditions used to prepare Mo doped VO₂ from the APCVD reaction of VOCl₃, H₂O and MoCl₅. Gas phase amount of H₂O was 0.026 mol min⁻¹.

All of the thin films of molybdenum doped vanadium(IV) oxide were dark yellow in colour and showed adherence properties comparable to those of the undoped vanadium(IV) oxide thin films prepared under the same conditions. The films passed the Scotch tape test and they could be removed by vigorous rubbing with a tissue. The films could be scratched with a brass stylus and a steel scalpel.

The molybdenum(V) chloride precursor was prone to blockages, especially in the mixing chamber and the reactor inlet. This resulted in films with a lower amount of molybdenum than anticipated and limited the maximum attained molybdenum content in the vanadium(IV) oxide thin films to approximately 1 atom%.

X-ray diffraction of the molybdenum doped vanadium oxide thin films (Figure 65) gave reflections at 27.8° and 57.6°, corresponding to the (011) and (022) planes of
4. APCVD of metal doped vanadium(IV) oxide

the vanadium(IV) oxide lattice. This indicated that there was some preferred orientation along (011). Significantly, no reflections due to oxides of molybdenum were observed in any of the XRD patterns suggesting that the molybdenum did not form a separate oxide phase in the thin film.

![XRD pattern](image)

Figure 65. XRD pattern of a 1 atom\% Mo doped VO$_2$ thin film prepared from the APCVD reaction of VOCl$_3$, H$_2$O and MoCl$_5$ at 650 °C. Also shown is a literature match pattern for VO$_2$(M).

The Raman spectrum of the molybdenum containing vanadium oxide thin films (Figure 66) showed bands at 192, 222, 260, 307, 338, 390, 492, and 610 cm$^{-1}$, which are all ± 2 cm$^{-1}$ of the Raman bands for undoped vanadium(IV) oxide described in sections 2.3.1.1 and 2.3.1.2. Raman bands for molybdenum(IV) oxide$^{111}$ are reported to occur at 365, 505, 595, 760 and 935 cm$^{-1}$ similar to those of the low temperature phase of vanadium(IV) oxide, which share the same monoclinic structure. No shoulders, excessive broadening or additional peaks were observed in the Raman spectra for molybdenum doped vanadium(IV) oxide, which would have occurred if molybdenum(IV) oxide was present as a separate phase. Raman bands for molybdenum(VI) oxide, which are reported to occur at 125, 158, 237, 283, 665, 817, 950, and 998 cm$^{-1}$,$^{111}$ were also not observed. This suggested that the molybdenum did not form a separate oxide phase but formed a solid solution in the vanadium oxide lattice.
4. APCVD of metal doped vanadium(IV) oxide

![Raman spectrum of a 1 atom% Mo doped VO$_2$ thin film](image)

Figure 66. Raman spectrum of a 1 atom% Mo doped VO$_2$ thin film prepared from the APCVD reaction of VOCl$_3$, H$_2$O and MoCl$_5$ at 650 °C.

Scanning electron microscopy revealed a particulate morphology for the molybdenum doped vanadium(IV) oxide thin films with particle sizes of 25 to 150 nm as shown in Figure 67. The film formation consisted of island aggregates of the particles on the substrate, with a typical film thickness of 300 nm as shown in Figure 68. This was consistent with a thin film rapidly grown on a highly nucleating substrate.

![SEM of Mo doped VO$_2$ thin film on glass](image)

Figure 67. SEM of Mo doped VO$_2$ thin film on glass prepared from the APCVD reaction of VOCl$_3$, H$_2$O and MoCl$_5$ at 650 °C.
4. APCVD of metal doped vanadium(V) oxide

Figure 68. Side-on SEM of Mo doped VO₂ thin film prepared from the APCVD reaction of VOCl₃, H₂O and MoCl₅ at 650 °C.

Figure 69. Deconvoluted Mo₃d XPS peaks for a Mo doped VO₂ thin film prepared from the APCVD reaction of VOCl₃, H₂O and MoCl₅ at 650 °C.

<table>
<thead>
<tr>
<th>Name</th>
<th>Pos.</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo 3d3/2</td>
<td>233.59</td>
<td>4.031</td>
</tr>
<tr>
<td>Mo 3d5/2</td>
<td>230.24</td>
<td>5.011</td>
</tr>
</tbody>
</table>
X-ray photoelectron spectroscopy was used to determine the composition of the molybdenum doped vanadium(IV) oxide thin films (Table 6), and to elucidate the oxidation states of the metal ions present in the material. Broad range survey spectra of the surface of the films showed the presence of vanadium, oxygen, molybdenum, carbon, silicon and nitrogen. The signals assigned to carbon, nitrogen could be attributed to atmospheric contaminants. The signal assigned to silicon was due the substrate as described in section 2.3.1. Figure 69 shows the Mo3d XPS region for a molybdenum doped vanadium(IV) oxide thin film. The 3d_{3/2} and 3d_{5/2} electrons of molybdenum gave weak, broad signals that were difficult to resolve so only tentative oxidation state assignments could be made. Deconvolution of the Mo3d XPS peak gave a 3d_{3/2} binding energy of 230.2 eV and a 3d_{5/2} binding energy of 233.6 eV. These values corresponded to literature values of molybdenum in the dioxide, and so the molybdenum may have been present as Mo^{4+} in the vanadium(IV) oxide lattice. This suggested a reduction of the molybdenum occurred during the deposition process from the molybdenum(V) chloride precursor. Comparison with the results from tungsten and chromium doping, and the formation of vanadium(IV) oxide from vanadium(V) oxytrichloride, shows that the reduction of transition metal precursors to lower valence oxides can be readily achieved in the APCVD process and is not inconceivable in the case of molybdenum doping. The XPS peaks at about 241 and 243 eV are the Ar2p_{3/2} and Ar2p_{1/2} XPS peaks respectively. Argon can be detected in films that have been argon ion etched due to implantation of the high-energy argon ions used to sputter the film material.

Deconvolution of the O1s and V2p_{3/2} XPS peaks for a molybdenum doped vanadium(IV) oxide thin film revealed that oxygen was present in two environments, bound to silicon with an O1s binding energy of 532.0 eV and bound to a vanadium or molybdenum with a O1s binding energy of 530.5 eV. Vanadium was also found to be present in two oxidation states, V^{4+} and V^{5+}, with V2p_{3/2} binding energies of 515.9 and 513.8 eV respectively. The discussion regarding the oxidation states in the molybdenum doped vanadium(IV) oxide thin films will be similar to that of tungsten doping of the vanadium(IV) oxide thin films. The reduction of the molybdenum species will probably have occurred at a different site.
4. APCVD of metal doped vanadium(IV) oxide

to film nucleation. Reduction of molybdenum in the presence of V\textsuperscript{4+} would probably result in the oxidation of the vanadium to V\textsuperscript{5+}, which would have been discernable by XPS.

![Deconvoluted O1s and V2p\textsubscript{3/2} XPS peaks for a Mo doped VO\textsubscript{2} thin film prepared from the APCVD reaction of VOCl\textsubscript{2}, H\textsubscript{2}O and MoCl\textsubscript{3} at 650 °C](image)

**Table 6**

<table>
<thead>
<tr>
<th>Name</th>
<th>Pos.</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1s (O=O)</td>
<td>532.05</td>
<td>2.037</td>
</tr>
<tr>
<td>O1s (O=O)</td>
<td>530.50</td>
<td>2.037</td>
</tr>
<tr>
<td>V2p\textsubscript{3/2} (V=O)</td>
<td>515.87</td>
<td>2.062</td>
</tr>
<tr>
<td>V2p\textsubscript{3/2} (V=O)</td>
<td>513.79</td>
<td>2.062</td>
</tr>
</tbody>
</table>

4.3.2.2 Thermochromic Properties.

The thermochromic properties of the molybdenum doped vanadium(IV) oxide thin films were analysed by Raman spectroscopy, infrared transmittance and visible/IR reflectance-transmittance.

The thermochromic transition temperature of the molybdenum doped vanadium(IV) oxide did not appear to be related to the concentration of molybdenum in the thin films, as shown in Table 6 and Figure 71. The highest molybdenum content would be expected to give the lowest transition temperature, which was not the case. The highest molybdenum content did not give the lowest transition temperature. A reason for this may have been that the oxidation state of the molybdenum did not affect the antiferroelectric distortion of the vanadium(IV)
4. APCVD of metal doped vanadium(IV) oxide

oxide band structure to cause a decrease in the metal-to-semiconductor transition temperature. The oxidation state of molybdenum introduced into vanadium(IV) oxide by sol-gel and PVD has not been reported. Molybdenum has been shown to cause a decrease in the thermoehromic transition temperature of vanadium(IV) oxide in films prepared by these methods. If the oxidation state of molybdenum is Mo\textsuperscript{6+} in these films then this may account for the difference observed in the films prepared by APCVD with molybdenum in the +4 oxidation state. No other explanation is apparent.

![Graph showing infrared switching at 2.5 μm and hysteresis curves for VO\textsubscript{2} thin films doped with 0.13, 0.4, and 1.0 atom% Mo prepared from the APCVD reaction of VOCl\textsubscript{2}, H\textsubscript{2}O and MoCl\textsubscript{5} at 650 °C.](image)

Figure 71. Infrared switching at 2.5 μm and hysteresis curves for VO\textsubscript{2} thin films doped with 0.13, 0.4, and 1.0 atom% Mo prepared from the APCVD reaction of VOCl\textsubscript{2}, H\textsubscript{2}O and MoCl\textsubscript{5} at 650 °C.

The transmittance properties of the molybdenum doped vanadium(IV) oxide films showed the changes typical of thin films of the undoped material as shown in Figure 72. A large decrease of 25 % was observed in the infrared region of the transmittance spectrum of the films when heated to above the transition temperature. There was no significant change in the visible region of the transmittance spectrum between the two states.
4. APCVD of metal doped vanadium(IV) oxide

4.3.3.1 Film Preparation and Characterisation.

Niobium(V) chloride was introduced into the vanadium(V) oxytrichloride and water APCVD system in an attempt to prepare niobium doped vanadium(IV) oxide thin films on glass substrates. The niobium(V) chloride precursor was found to be very prone to condensing out of the gas phase and blocking the APCVD apparatus. This was partially overcome by applying additional heating around the coolest section of the apparatus to maintain the precursor in the gas phase for introduction into the CVD reactor. Only one successful sample was made in which niobium was detected in the vanadium oxide thin film. Analysis of this film is given in this section, but only tentative conclusions can be drawn.

The conditions used to prepare the niobium doped vanadium(IV) oxide thin film are given in Table 7.
4. APCVD of metal doped vanadium(IV) oxide

<table>
<thead>
<tr>
<th>Reactor Temperature / °C</th>
<th>Gas phase amount NbCl₅ / mol min⁻¹</th>
<th>Gas phase amount VOCl₃ / mol min⁻¹</th>
<th>Gas phase amount H₂O / mol min⁻¹</th>
<th>Phase from XRD and Raman</th>
<th>Nb content in film / atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>0.056</td>
<td>0.053</td>
<td>0.026</td>
<td>VO₅(M)</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Table 7. Conditions used for the preparation of a Nb doped VO₂ thin film from the APCVD reaction of VOCl₃, H₂O and NbCl₅.

The X-ray diffraction pattern for the niobium doped vanadium(IV) oxide thin film showed reflections at 27.8° and 57.5°, corresponding to the (011) and (022) planes of monoclinic vanadium(IV) oxide respectively. This indicated that the niobium doped vanadium(IV) oxide thin film was preferentially orientated along the (011) plane. No reflections for niobium oxides were observed, suggesting the niobium did not form a separate phase in the thin film but was incorporated as a solid solution in the vanadium(IV) oxide lattice.

The Raman spectrum of the niobium doped vanadium(IV) oxide thin film showed bands at 192, 222, 261, 309, 339, 390, 441, 479, 497, and 611 cm⁻¹. All of these
bands are ±2 cm$^{-1}$ of those for undoped vanadium(IV) oxide, as described in section 2.3.1. Niobium(V) oxide has very broad Raman bands occurring at 129, 329, and 706 cm$^{-1}$, which were not observed in the niobium doped vanadium(IV) oxide thin film, suggesting the niobium formed a solid solution with the vanadium oxide.

![Raman spectrum for 0.4 atom% Nb doped VO$_2$ on glass prepared from the APCVD reaction of VOCl$_2$, H$_2$O and NbCl$_5$ at 650 °C.](image)

Scanning electron microscopy (Figure 75) revealed a randomly orientated, rod-like morphology to the niobium doped vanadium(IV) oxide thin film, interspersed with particulates. The rods were 1-2 μm long and 150-400 nm in width and the particulates were approximately 250 nm in diameter. There appeared to be no significant differences in the composition between the rod-like structures and the particulates when analysed by EDX and backscattered SEM. The particulates were likely to have been formed in gas-phase reactions and then deposited on to the substrate.
4. APCVD of metal doped vanadium(V) oxide

Figure 75. SEM of 0.4 atom% Nb doped VO$_2$ thin film prepared from the APCVD reaction of VOCl$_3$, H$_2$O and NbCl$_5$ at 650°C.

Figure 76. Deconvoluted XPS spectrum of the Nb3d peaks for a 0.4 atom% Nb doped VO$_2$ thin film prepared from VOCl$_3$, H$_2$O and NbCl$_5$ at 650°C.
4. APCVD of metal doped vanadium(IV) oxide

X-ray photoelectron spectroscopy was used to determine the composition of the niobium doped vanadium(IV) oxide thin film and to reveal the oxidation states of the ions present in the material. Broad range survey XPS analysis of the surface of the thin film showed vanadium, oxygen, niobium, nitrogen, silicon, and carbon to be present. The sources of the nitrogen, silicon and carbon have been detailed in previous sections.

Deconvolution of the Nb3d region of the XPS spectrum gave Nb3d5/2 and Nb3d3/2 binding energies of 207.1 and 209.8 eV respectively. These values corresponded to the binding energies found for niobium in Nb2O5. This suggested that the niobium was present as Nb5+, and that the niobium ions did not undergo a reduction during the CVD process. This is unlike the other transition metal dopants reported so far in this thesis.

![Deconvoluted O1s-V2p XPS peaks for a 0.4 atom% Nb doped VO2 prepared from the APCVD reaction of VOCl3, H2O and NbCl3 at 650°C.](image)

Figure 77. Deconvoluted O1s-V2p XPS peaks for a 0.4 atom% Nb doped VO2 prepared from the APCVD reaction of VOCl3, H2O and NbCl3 at 650°C.
Deconvolution of O1s and V2p region of the XPS spectrum gave a V2p½ binding energy of 515.9 eV, corresponding to V\(^{5+}\), no V\(^{3+}\) was determined to be present. The O1s XPS peak could be deconvoluted to two peaks with binding energies of 530.6 and 532.5 eV. The peak at 530.6 eV could be assigned to oxygen bound to a transition metal ion. The peak at 532.5 eV could be assigned to oxygen bound to silicon as in the glass substrate, detectable through pinhole defects in the thin film.

4.3.3.2 THERMOCHROMIC PROPERTIES.

The thermochromic properties of the niobium doped vanadium(IV) oxide thin film were investigated by IR transmittance and visible/IR reflectance-transmittance. The IR transmittance hysteresis curve for the niobium doped vanadium(IV) oxide thin film is shown in Figure 78. The thermochromic transition temperature was determined to be 55 ± 5 °C. This represents a decrease of 13 °C in the thermochromic transition temperature from the undoped material. The hysteresis width and the sharpness of the transition were comparable to those observed for tungsten doped vanadium(IV) oxide described in section 3.3.

![Figure 78. Hysteresis curve of the IR (2.5 mm) transmittance for a 0.4 atom% Nb doped VO\(_2\) prepared from the APCVD reaction of VOCl\(_4\), H\(_2\)O and NbCl\(_5\) at 650 °C.](image-url)
4. APCVD of metal doped vanadium(IV) oxide

The reflectance and transmittance spectra above and below the thermochromic transition temperature for the niobium doped vanadium(IV) oxide thin film are shown in Figure 79. Quite substantial differences in the spectra were observed when passing between the two states. The transmittance spectrum for the low temperature phase of the niobium doped vanadium(IV) oxide thin film showed an increasing transmittance with increasing wavelength. The transmittance in the visible region was lower than for undoped and tungsten doped vanadium(IV) oxide thin films. Above the thermochromic transition temperature the visible transmittance was typical of vanadium(IV) oxide thin films. There was also a marked decrease in the infrared transmittance above the thermochromic transition temperature. The reflectance spectra showed an increase in reflectance with increasing wavelength, but above the thermochromic transition temperature the infrared reflectance was significantly increased. This indicated that niobium doped vanadium(IV) oxide thin films prepared by this APCVD method could fulfil the requirements for intelligent window coatings if the niobium content was increased to the extent that the thermochromic transition temperature of the material was lowered to about 25 °C.

Figure 79. Reflectance-transmittance spectra for a 0.4 atom% Nb doped VO₂ thin film prepared from the APCVD reaction of VOCl₃, H₂O and NbCl₅ at 650 °C.
4.3.4 APCVD of \( \text{VOCI}_3, \text{H}_2\text{O} \) and \( \text{TiCl}_4 \)^15

4.3.4.1 FILM PREPARATION AND CHARACTERISATION.

The final transition metal dopant to be added to the vanadium(IV) oxide lattice was titanium. Thin films of titanium containing vanadium(IV) oxide were prepared by introducing titanium(IV) chloride into the vanadium(V) oxytrichloride and water system using the conditions developed in section 2.3.2.1. The conditions used in the production of titanium containing vanadium(IV) oxide are shown in Table 8. The introduction of titanium(IV) chloride into the vanadium(V) oxytrichloride and water system gave some unusual results. The X-ray diffraction of these thin films (Figure 80) all gave a strong reflection at 27.8 ° corresponding to the (011) reflection of monoclinic vanadium(IV) oxide, suggesting that the films had a preferred orientation on the substrate.

<table>
<thead>
<tr>
<th>Substrate Temperature/ °C</th>
<th>Gas phase amount ( \text{VOCI}_3 )/ mol min(^{-1} )</th>
<th>Gas phase amount ( \text{TiCl}_4 )/(mol min(^{-1} ))</th>
<th>Gas phase amount ( \text{H}_2\text{O} )/ mol min(^{-1} )</th>
<th>Phase observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>0.074</td>
<td>0.0001</td>
<td>0.026</td>
<td>( \text{VO}_2 )</td>
</tr>
<tr>
<td>650</td>
<td>0.053</td>
<td>0.0004</td>
<td>0.026</td>
<td>( \text{VO}_2 )</td>
</tr>
<tr>
<td>650</td>
<td>0.018</td>
<td>0.0008</td>
<td>0.026</td>
<td>( \text{VO}_2 )</td>
</tr>
<tr>
<td>650</td>
<td>0.040</td>
<td>0.0007</td>
<td>0.026</td>
<td>( \text{VO}_2 )</td>
</tr>
<tr>
<td>650</td>
<td>0.030</td>
<td>0.0010</td>
<td>0.026</td>
<td>( \text{VO}_2 )</td>
</tr>
<tr>
<td>600</td>
<td>0.035</td>
<td>0.0014</td>
<td>0.026</td>
<td>0.9( \text{VO}_3 ), 0.1 ( \text{TiO}_2 )</td>
</tr>
<tr>
<td>550</td>
<td>0.018</td>
<td>0.0013</td>
<td>0.026</td>
<td>0.9( \text{VO}_3 ), 0.1 ( \text{TiO}_2 )</td>
</tr>
</tbody>
</table>

Table 8. Conditions used for the preparation of Ti containing \( \text{VO}_2 \) thin films from the APCVD reaction of \( \text{VOCI}_3, \text{H}_2\text{O} \) and \( \text{TiO}_2 \).

Films prepared with a reactor temperature of 650 °C did not contain titanium when analysed by EDX and XPS. When the exhaust was examined a white deposit of titanium(IV) oxide was discovered, confirming that titanium(IV) chloride was introduced into the reactor. The reaction of titanium(IV) chloride and water is very fast and requires lower substrate temperatures in an APCVD reaction, in which are formed hazy, particulate films.\(^{15}\) It was assumed that particles of titanium(IV) oxide
4. APCVD of metal doped vanadium(IV) oxide

were produced in the gas phase that were then carried out of the reactor in the gas stream. Titanium(IV) oxide, formed from titanium(IV) chloride, is in fact often used as a gas flow indicator in CVD reactor systems. Attempts were made to introduce titanium into the vanadium(IV) oxide lattice by reducing the substrate temperature, as shown in Table 8.

![Figure 80. XRD of VO₂ thin film prepared from VOCl₃ and H₂O in the presence of TiCl₄ at 650 °C. Also shown is a literature match pattern for VO₂(M).](image)

![Figure 81. SEM of VO₂ thin film prepared from VOCl₃ and H₂O in the presence of TiCl₄.](image)
4. APCVD of metal doped vanadium(IV) oxide

The films prepared at a reactor temperature of 650 °C were not without interest. The morphology of these films was significantly different from those of films prepared with other precursor systems described in this thesis. The introduction of titanium(IV) chloride causes the films to develop a spherical structure with diameters of 150-200 nm as shown in Figure 81. A possible explanation for this is that the titanium(IV) oxide particles in the gas stream act as a template for the change in morphology observed.

![Figure 82. Raman spectrum for a composite TiO_2/VO_2 thin film prepared from the APCVD reaction of VOCl_3, H_2O and TiCl_4.](image)

When the reactor temperature is reduced to 600 and 550 °C titanium could be introduced into the vanadium(IV) oxide thin film. X-ray diffraction showed one reflection at 27.8 °C corresponding to the (011) plane of monoclinic vanadium(IV) oxide. No reflections due to titanium(IV) oxide were observed in the XRD pattern. Raman spectroscopy, however, showed bands at 143, 191, 222, 298, 393, 497 and 611 cm\(^{-1}\) (Figure 82). The band at 143 cm\(^{-1}\) (labelled * in Figure 82) could be assigned to the \(E_g\) mode of anatase titanium(IV) oxide. The remaining bands could be assigned to the monoclinic phase of vanadium(IV) oxide. This suggested that a composite film of vanadium(IV) oxide and titanium(IV) oxide was formed, not a solid solution of titanium in vanadium(IV) oxide.
4. APCVD of metal doped vanadium(IV) oxide

Scanning electron microscopy revealed thin films composed of two distinct types of particle. A worm-like structure was observed along with spherical particles, as illustrated in Figure 83. The worm-like structure was similar to that observed with tungsten doped vanadium(IV) oxide thin films described in section 3.3.2.1. Spot EDX analysis showed that the worm-like particles were vanadium rich, while the spherical particles were titanium rich. The wide area EDAX analysis showed that the films were composed of one part titanium(IV) oxide to nine parts vanadium(IV) oxide. The absence of XRD reflections due to titanium(IV) oxide indicated that the spherical particles of titanium(IV) oxide were probably amorphous.

X-ray photoelectron spectroscopy of the composite vanadium(IV) oxide and titanium(IV) oxide thin films showed peaks assigned to vanadium, oxygen, titanium, silicon, carbon and nitrogen. The presence of silicon, carbon and nitrogen has been discussed in previous sections. Vanadium was found to be nine times more abundant in the films than titanium. This was in agreement with the EDX results. Deconvolution of the Ti2p$\text{\textsubscript{3/2}}$ XPS region (Figure 84) gave one peak with a binding energy of 458.7 eV, corresponding to Ti$^{4+}$ in TiO$_2$.
4. APCVD of metal doped vanadium(V) oxide

Figure 84. Deconvoluted Ti 2p3/2 XPS peak for a composite VO2/TiO2 thin film prepared from the APCVD reaction of VOCl3, H2O and TiCl4 at 550 °C.

Figure 85. Deconvoluted O 1s and V 2p3/2 XPS peak for a composite VO2/TiO2 thin film prepared from the APCVD reaction of VOCl3, H2O and TiCl4 at 550 °C.
Deconvolution of the V\textsubscript{2p\textsubscript{3/2}} region gave one peak with a binding energy of 515.9 eV, corresponding to V\textsuperscript{3+} cations. Deconvolution of the O\textsubscript{1s} XPS region gave peaks with binding energies of 532.1 and 530.4 eV. The peak at 532.1 eV corresponded to oxygen bound to silicon. The peak at 530.4 eV could be assigned to oxygen in a transition metal oxide.

4.3.4.2 THERMOCHROMIC PROPERTIES.

The thermochromic transition temperature was measured for the TiO\textsubscript{2}–VO\textsubscript{2} films at 55 °C (Figure 86). This is a decrease from that of pure VO\textsubscript{2} films and is most probably related to the morphology of the VO\textsubscript{2} films, which have one axis that that is ca 100 nm in dimension and hence is likely to have some induced strain. The change in morphology to a spherical structure also affected the thermochromic transition temperature of the films not containing titanium. Films with this morphology exhibited a thermochromic transition temperature of 45 °C, a 24 °C decrease from that typically observed for bulk and thin film vanadium(IV) oxide. As no titanium was detected in the films, the difference in switching temperature must arise from the change in morphology of the VO\textsubscript{2} films. The presence of strain effects, as described in section 1.6, is the likely explanation for this observation.

Figure 86. Hysteresis curves of the IR (2.5 mm) transmittance for (a) composite TiO\textsubscript{2}–VO\textsubscript{2} thin film and (b) VO\textsubscript{2} thin film with spherical morphology; prepared from the APCVD reaction of VOCl\textsubscript{3}, H\textsubscript{2}O and TiCl\textsubscript{4}. 129
As the presence of titanium(IV) oxide particles were detected, the photocatalytic activity and photo-induced superhydrophilicity of the composite films were investigated. For the films prepared at a substrate temperature of 600 °C the initial water contact angle was 73 °, this reduced to 21 ° on exposure to 254 nm radiation for 1 h and decreased further to 14.6 ° after 24 hours exposure to sunlight. Leaving the films in the dark for 24 h caused an increase in contact angle to 54 °. With the films prepared with a reactor temperature of 550 °C, the initial water contact angle of 73 ° decreased to 48 ° after 1h illumination with 254 nm radiation and then went down further to 35 ° after 24 hours exposure to sunlight. Storage in the dark caused an increase in the water contact angle to 60 °. The variations in contact angle are readily explained by the TiO₂ component of the films. Anatase titanium(IV) oxide is an excellent photocatalyst that also exhibits photoinduced superhydrophilicity.° Indeed water contact angles of less than 5 ° are often observed for a pure anatase film.° The proposed mechanism for the lowering of the contact angle involves the formation of UV induced reduced Ti(III)-O-H terminated surface that can readily hydrogen bond to water. On storage in the dark in air the films will slowly reoxidise in air to a Ti(IV)-oxo terminated surface that is not as hydrophilic - and hence the contact angle increases.° The composite films formed in this study only contain ca 10% TiO₂ however this is sufficient to allow the surface to show very low contact angles.

The photocatalytic results are also indicative of small amounts of titanium(IV) oxide incorporated into the film. After 180 min of UV irradiation (254 nm), the peak area of the C-H stretch of a stearic acid overlayer was reduced by nearly 30%, as shown in Figure 87.
4. APCVD of metal doped vanadium(IV) oxide

4.3.5 APCVD of VCl₄, H₂O and SnCl₂

4.3.5.1 Film preparation and characterisation.

The final system investigated in this work was to prepare tin doped vanadium(IV) oxide thin films by the APCVD reaction of vanadium(IV) chloride, water and tin(IV) chloride. The conditions used to prepare tin containing vanadium oxide thin films are given in Table 9.

X-ray diffraction of thin films prepared with the inclusion of tin(IV) chloride in the reaction system showed that the predominant phase of the film was tin(IV) oxide. Vanadium was detected by EDX but no phases of vanadium oxide were revealed in the XRD pattern as shown in Figure 88. Raman spectroscopy of these thin films (Figure 89) showed bands at 479, 564, 638, and 781 cm⁻¹, which can be assigned to \( E_g \), \( S_1 \), \( A_{1g} \) and \( B_2g \) modes of tin(IV) oxide respectively.¹¹⁶ The amounts of tin(IV) chloride introduced were the lowest possible. The bubbler was at ambient temperature and the minimum flow rate was used. This suggested that the tin(IV)
chloride was much more reactive in the CVD system than vanadium(IV) chloride and preferentially deposited oxides of tin over oxides of vanadium.

<table>
<thead>
<tr>
<th>Reactor temperature / °C</th>
<th>Gas phase amount SnCl₄ / mol min⁻¹</th>
<th>Gas phase amount VCl₄ / mol min⁻¹</th>
<th>Gas phase amount H₂O / mol min⁻¹</th>
<th>Phase</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.00065</td>
<td>0.0047</td>
<td>0.048</td>
<td>SnO₂</td>
<td>0.01 atom% V</td>
</tr>
<tr>
<td>600</td>
<td>0.00035</td>
<td>0.0034</td>
<td>0.048</td>
<td>SnO₂</td>
<td>0.01 atom% V</td>
</tr>
<tr>
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<td>contaminant</td>
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<td>0.048</td>
<td>VₓOₓ(Mₓ) /SnO₂</td>
<td>15 atom% Sn</td>
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Table 9. Reaction conditions for the preparation of tin containing vanadium(IV) oxide thin films from the APCVD reaction of VCl₄, H₂O and SnCl₄.

Figure 88. XRD of a thin film prepared from the APCVD reaction of VCl₄, H₂O and SnCl₄ at 600 °C. Also shown is a literature match pattern for SnO₂.
4. APCVD of metal doped vanadium(V) oxide

Figure 89. Raman spectrum for a thin film prepared from VCl₄, H₂O and SnCl₂ at 600 °C

Figure 90. XRD pattern of a composite SnO₂:VO₂ thin film on glass prepared from the APCVD reaction of VCl₄, H₂O and residual amounts of SnCl₂ at 625 °C. Also shown are literature match patterns for VO₂(M) (44-0252) and SnO₂ (41-1445). * Unassigned reflections
Even if the amount of tin(IV) chloride was of contaminant level, from residues remaining in the connective pipe work, the reactivity of tin(IV) chloride was such that separate phases of vanadium(IV) oxide and tin(IV) oxide were observed as shown in the XRD pattern of Figure 90. A slight shift in the positions of the tin(IV) oxide reflections to higher 2θ values was observed. This may have been caused by a distortion of the tin(IV) oxide lattice due to presence of vanadium.

Raman spectroscopy of this contaminated film (Figure 91) showed Raman bands at 144, 192, 222, 263, 307, 339, 391, 441, 498, and 614 cm⁻¹. These bands correspond to those of the monoclinic phase of vanadium(IV) oxide, Raman bands for tin(IV) oxide were masked by those of vanadium(IV) oxide and so were not observed.

Scanning electron microscopy (Figure 92) revealed a particulate morphology for all of the tin containing thin films with particle sizes of about 50 nm that aggregated into islands with a dimension of about 200 nm. Side-on SEM (Figure 93) showed the film thickness to be between 400 nm and 500 nm, and a columnar structure was revealed for the particle aggregates. EDX area mapping revealed that tin was distributed throughout the films. It was not possible to observed any areas that were concentrated with tin on the contaminated vanadium(IV) oxide thin films.
suggesting that the feature sizes were smaller than the sampling spot size of the electron beam probe.

Figure 92. SEM of a thin film prepared from the APCD reaction of VCl₃, H₂O and SnCl₄ at 600 °C.

Figure 93. Side-on SEM of a thin film prepared from the APCVD reaction of VCl₃, H₂O and SnCl₄ at 600 °C.
4. APCVD of metal doped vanadium(IV) oxide

4.3.5.2 THERMOCHROMIC PROPERTIES.

The thermochromic properties of vanadium(IV) oxide thin films contaminated by tin(IV) oxide were investigated by reflectance and transmittance spectroscopy. Figure 94 shows the hysteresis curve for the transmittance at 2.5 μm of a tin(IV) oxide contaminated (15 atom% tin) vanadium(IV) oxide thin film. The thermochromic transition temperature for this film was determined to be 60 °C, only 8 °C lower than for an undoped vanadium(IV) oxide thin film. This indicated that even very high amounts of tin had only a small effect on the temperature at which the thermochromic transition occurred. This may even have been the result of strain-induced effects due to the composite nature of the thin films. The optical contrast between the low temperature and high temperature phase was only about 15%, much less than for other doped vanadium(IV) oxide thin films described in this thesis. This was the result of the phase segregated tin(IV) oxide present in the film, which does not display a metal-to-semiconductor phase transition. Infrared radiation was still be able to pass through the tin(IV) oxide phase of the thin film even after the vanadium(IV) oxide phase had undergone the thermochromic phase transition. The width of the hysteresis is narrow compared to thin films of vanadium(IV) oxide doped with other metal ions described in this thesis.

![Figure 94. Hysteresis curve of the IR (2.5 mm) transmittance for a composite SnO₂:VO₂ thin film on glass prepared from the APCVD reaction of VCl₄, H₂O and residual amounts of SnCl₄ at 625 °C.](image-url)
4. APCVD of metal doped vanadium(IV) oxide

The reflectance and transmittance spectra below and above the thermochromic transition temperature of the tin(IV) oxide contaminated vanadium(IV) oxide thin film is shown in Figure 95. The appearance of the spectra for the low temperature phase was typical of vanadium(IV) oxide. The changes in the spectra when the temperature was increased to above the thermochromic transition temperature were not as dramatic as for other doped vanadium(IV) oxide thin films and were a consequence of the phase separated nature of the thin film, as discussed above.

4.4 Conclusions and further discussion

This chapter has described the preparation and analysis of vanadium(IV) oxide thin films doped with a selection of metal ions. Thin films prepared from the APCVD reaction of vanadium(V) oxytrichloride, water and chromium(VI) oxychloride did not produce chromium doped vanadium(IV) oxide. Instead thin films of a chromium vanadium oxide were formed which appeared to have a structure related to Cr₂O₃ and XCr₂O₃ (X = Na, K, Rb). These films did not display any thermochromic properties but they may find use as electrode materials in solid-state batteries.
4. APCVD of metal doped vanadium(IV) oxide

The introduction of molybdenum(V) chloride into the vanadium(V) oxytrichloride precursor system yielded promising results. Molybdenum doped vanadium(IV) oxide thin films were prepared, with molybdenum concentrations of up to 1 atom% molybdenum achieved. These films showed reduced thermochromic transition temperatures compared to the undoped material. The lowest transition temperature observed was 47 °C for a 0.3 atom% molybdenum doped film. A clear relationship between molybdenum concentration and transition temperature was not observed. This was possibly due to the oxidation state of the molybdenum ions in the vanadium(IV) oxide lattice. The Mo$^{4+}$ ions may not have affected the stabilisation of the monoclinic phase of vanadium(IV) oxide in a consistent manner, making the change in transition temperature unpredictable. The maximum molybdenum loading of the thin films was limited by the transport properties of the molybdenum(V) chloride precursor. The molybdenum doped vanadium(IV) oxide thin films showed optical properties that were suitable for use as an intelligent window coating.

Niobium doping of vanadium(IV) oxide from the APCVD reaction of vanadium(V) oxytrichloride, water and niobium(V) chloride was also attempted. This precursor system suffered from similar disadvantages to those found with the use of molybdenum(V) chloride. A thin film of vanadium(IV) oxide was prepared containing 0.4 atom% niobium that showed a thermochromic transition temperature of 55 °C and optical properties such as those required for intelligent window coatings. Niobium doping into vanadium(IV) oxide was interesting as, unlike other transition metal dopants used in this thesis, the niobium ions were not reduced during the deposition process and remained in the +5 oxidation state of the precursor.

Titanium(IV) chloride, when introduced into the vanadium(V) oxytrichloride and water system gave some extraordinary results. At a reactor temperature of 650 °C, typically required for the formation of vanadium(IV) oxide from the APCVD reaction of vanadium(V) oxytrichloride and water, no titanium was incorporated into the vanadium(IV) oxide thin films. The presence of titanium(IV) oxide particles in the gas stream had a profound effect on the morphology of the thin film. Instead of the usual particulate morphology of the vanadium(IV) oxide thin
films, spherical structures were observed. This morphology caused a stress induced decrease in the thermochromic transition temperature of 24 °C. When the reactor temperature was lowered to 600 and 550 °C, a phase segregated vanadium(IV) oxide and titanium(IV) oxide thin film was formed that showed multifunctional properties of thermochromism, photo-induced superhydrophilicity and photocatalytic activity.

A phase segregated thin film of vanadium(IV) oxide and tin(IV) oxide could be prepared when tin(IV) chloride was added to the vanadium(IV) chloride and water APCVD precursor system. The tin(IV) chloride was much more reactive than the vanadium(IV) chloride and if too much was introduced the tin(IV) oxide predominated. The tin containing vanadium(IV) oxide thin films showed slightly reduced thermochromic transition temperatures but the multiphase film was not entirely suitable for intelligent window coating applications due to a poor contrast between the infrared transparent and reflective states.

There was a disparity between the vanadium oxide thin films containing tungsten, molybdenum or niobium, those containing chromium or tin and those containing titanium. There were comparable amounts of dopant precursor introduced into the CVD reaction systems. The first group of dopants appeared to form solid-solutions with the vanadium(IV) oxide lattice and caused a decrease in the thermochromic transition temperature by disrupting the antiferroelectric distortion of the monoclinic phase. The second group of dopants formed films composed predominantly of the intended dopant material, with dopant levels of vanadium. This may indicate that in the APCVD system, chromium(VI) oxychloride and tin(IV) chloride were more reactive, and deposited oxide films more readily than vanadium(IV) chloride or vanadium(V) oxytrichloride. Even at contaminant amounts, tin(IV) chloride still formed tin(IV) oxide as a separate phase to vanadium(IV) oxide, indicating a high reactivity in the APCVD system.

Titanium(IV) chloride also appeared to be more reactive than vanadium(V) oxytrichloride in the APCVD system. Gas-phase reactions appeared to cause nucleation of titanium(IV) oxide particles, which were then deposited along with vanadium(IV) oxide thin films. The spherical structure of the titanium(IV) oxide particles in the films indicated that they were formed in a gas-phase reaction. It
4. APCVD of metal doped vanadium(IV) oxide

would be assumed that titanium and tin would readily form a solid solution with vanadium(IV) oxide. The dioxides of titanium and tin have a rutile structure related to the monoclinic structure of vanadium(IV) oxide so a lattice mismatch phenomenon is unlikely to be the cause of the phase segregation. The precursors that formed solid-solutions with the vanadium(IV) oxide lattice were all solids at room temperature. This may be a factor in preventing them from forming phase-segregated films. The solid precursors may have lower reactivities that could allow the reactive species to form on the substrate surface instead of in the gas phase. The surface species would then migrate to the vanadium oxide nucleating sites. A highly reactive liquid precursor may be more likely to undergo gas-phase nucleation or react quickly on the substrate surface to form a separate phase.
5. Conclusions

Chapter 5

CONCLUSIONS AND CONSIDERATIONS FOR FUTURE WORK.

5.1 Overall conclusions

This thesis has examined the use of the commercially important process of atmospheric pressure chemical vapour deposition to prepare thin films of single phase and metal doped vanadium(IV) oxide. This material has many potential technological applications and this thesis has concentrated on its use as an intelligent window coating.

Two precursor systems were used successfully to prepare thin films of vanadium(IV) oxide on glass substrates in the APCVD apparatus. Vanadium(IV) chloride and water produced vanadium(IV) oxide at reactor temperatures of greater than 550 °C and with a 5-10 times excess of water over vanadium(IV) chloride. These films were concentrated on the hotter, central leading edge area of the substrate. Towards the cooler regions of the substrate, closer to the walls of the cold-wall reactor, VO₃, a non-stoichiometric phase of vanadium oxide, was often observed. Below 550 °C vanadium(V) oxide was formed. This suggested a kinetically controlled deposition.

Vanadium(V) oxytrichloride and water formed vanadium(IV) oxide with reactor temperatures above 600 °C and a slight excess of water over vanadium(V) oxytrichloride. A mixed phase of V₂O₅ and V₆O₁₉ was formed towards the inlet end of the substrate with the vanadium(IV) oxide region towards the exhaust end. Adjusting the total gas flow-rate through the reactor could control the relative sizes of these regions. A total gas flow-rate of below 1 L min⁻¹ enabled almost complete coverage of the substrate with vanadium(IV) oxide. At reactor temperatures of 550 °C and below, or with an excess of vanadium(V) oxytrichloride over water, vanadium(V) oxide thin
films could be formed. A mass transport growth mechanism could be envisioned as the film thickness was not affected by variations in temperature across the substrate. The films were progressively thinner towards the exhaust end of the substrate.

The thin films of vanadium(IV) oxide prepared from these two systems showed the thermochromic response typical of single crystals of the material. The structural change from monoclinic to tetragonal was observed by Raman spectroscopy and X-ray diffraction to occur at 68 °C. The optical properties of the thin films were also typical of the bulk material. Below the transition temperature the films of vanadium(IV) oxide were visually and infrared transparent, but above the transition temperature the thin films became infrared reflective while remaining visually transparent. This was the ideal response of the films for the targeted use of intelligent window coatings.

Vanadium(IV) oxide was also deposited on silicon using the vanadium(V) oxytrichloride and water system. This opens up further technological uses for thin films of vanadium(IV) oxide prepared by APCVD, such as in data storage and infrared modulators. From the vanadium(IV) chloride and water system, a mixed phase thin film of vanadium(V) oxide and vanadium(IV) oxide was produced.

Tungsten doping of the vanadium(IV) oxide thin films was performed to reduce the thermochromic transition temperature to closer to room temperature and increase the commercial applicability of the APCVD process for intelligent window coatings. Tungsten doping was successfully achieved using two precursor systems. Tungsten(VI) ethoxide was introduced into the vanadium(IV) chloride and water system, which produced thin films of vanadium(IV) oxide containing up to 1.2 atom% tungsten. These thin films displayed thermochromic transition temperatures as low as 45 °C when measured by Raman spectroscopy, XRD and IR transmittance. The tungsten was found to have an oxidation state of W⁶⁺ in the vanadium(IV) oxide lattice and appeared to cause a change in the oxidation state of some of the vanadium cations from V⁴⁺ to V⁷⁺. The optical properties of the tungsten
doped vanadium(IV) oxide thin films were suitable for the target application, showing a vivid decrease in infrared transmittance and an increase in infrared reflectance when heated to above the thermochromic transition temperature. Tungsten(VI) chloride was introduced into the vanadium(V) oxytrichloride and water system to prepare tungsten doped vanadium(IV) oxide thin films. Thermochromic transition temperatures as low as 5 °C were observed with tungsten contents of 3 atom%. The tungsten was found to have an oxidation state of W⁴⁺ in the vanadium(IV) oxide lattice and appeared to cause a reduction of some of the V⁴⁺ cations to V³⁺. The optical properties of these tungsten doped vanadium(IV) oxide thin films were suitable for use as intelligent window coatings.

Other metal ions were introduced into the vanadium(IV) oxide lattice using the APCVD process. Chromium(VI) oxychloride was introduced into the vanadium(V) oxytrichloride system and produced thin films of a chromium vanadium oxide that appeared to have a similar structure to Cr₂O₃ and Cr₂O₅. These films did not show any thermochromic properties. Molybdenum doping was achieved by introducing molybdenum(V) chloride into the vanadium(V) oxytrichloride system. This produced vanadium(IV) oxide thin films with up to 1 atom% molybdenum and thermochromic transition temperatures of 47 °C. There appeared to be no correlation between the amounts of molybdenum in the thin films with the switching temperature. The +4 oxidation state of the molybdenum in the films may not have affected the antiferroelectric distortion of the monoclinic vanadium(IV) oxide and as such would not cause a large depression in the switching temperature.

Niobium doped vanadium(IV) oxide was prepared from vanadium(V) oxytrichloride, water and niobium(V) chloride. This system produced a thin film of vanadium(IV) oxide containing 0.4 atom% Nb⁵⁺ that showed a thermochromic transition temperature of 55 °C and changes in optical properties suitable for intelligent window coatings. Of the dopants that formed solid-solutions with vanadium(IV) oxide niobium was the only one
that appeared not to undergo a reduction from the precursor during the deposition.

Titanium(IV) chloride, when introduced into the vanadium(IV) oxide and water system, produced two types of thin film. At reactor temperatures of 650 °C an undoped thin film of vanadium(IV) oxide was produced that had a spherical morphology. These films displayed a thermochromic transition temperature of 45 °C, probably due to intrinsic strain in the particles. Gas-phase nucleation of titanium(IV) oxide particles could have acted as a template for the formation of the spherical morphology of the vanadium(IV) oxide. At reactor temperatures of 600 °C and 550 °C composite films with spherical particles of anatase titanium(IV) oxide and worm-like structures of vanadium(IV) oxide were formed. These films showed multifunctional properties. The vanadium(IV) oxide showed thermochromism with a transition temperature of 55 °C, and the titanium(IV) oxide showed photocatalytic activity and photoinduced superhydrophilicity.

Tin(IV) chloride was much more reactive than vanadium(IV) chloride with water and thin films of tin(IV) oxide containing vanadium were prepared when this system was attempted. Composite films of vanadium(IV) oxide and tin(IV) oxide were produced when contaminant levels of tin(IV) chloride were introduced into the vanadium(IV) chloride and water APCVD system. These composite films showed slightly reduced thermochromic transition temperatures probably due to strain-induced effects.

The films prepared with solid precursors for the dopant metals; W, Mo, Nb, showed apparent substitutional doping in the vanadium(IV) oxide lattice. The films prepared with liquid precursors for the dopant metals; Cr, Sn, Ti, gave films of the oxide of that metal doped with vanadium (V:Cr₂O₇ or V:SnO₂), or a phase segregated MO₃/VO₅ (M = Sn, Ti) composite film. This appeared to be related to the relative reactivities of the dopant precursors. Solid precursors reacted sufficiently slowly to allow the formation of vanadium(IV) oxide with which the dopant metal could integrate. Liquid dopant precursors reacted faster than the vanadium precursors creating vanadium doped metal
5. Conclusions

oxide thin films. Alternatively gas-phase reactions formed particles that then deposited along with the vanadium(IV) oxide. This was the case for titanium(IV) chloride; spherical particles of titanium(IV) oxide were observed in the vanadium(IV) oxide thin film.

5.2. Considerations for future work.

The work described in this thesis has demonstrated that undoped and doped vanadium(IV) oxide thin films can be prepared from the APCVD of halide precursors. Knowledge of the reaction mechanisms for the systems would be necessary to enable improvements to the depositions. This analysis may give an insight into how vanadium(IV) oxide is formed preferentially to other oxides of vanadium at higher substrate temperatures. Also information could be gained on where the reduction of the vanadium(V) oxytrichloride and the dopant precursors occurs. This may occur in the gas phase or on the substrate surface. Some investigations into the reaction mechanisms are being performed at the University of Salford. This will involve a spectroscopic analysis of the species present in the CVD reactor during deposition.

The application of colour suppressants and anti-reflective coatings to improve the visual appearance of the vanadium(IV) oxide thin films could be investigated. This would involve applying an additional coating over the vanadium(IV) oxide thin film to improve the luminous transmittance and shift the transmittance spectrum of the thin films towards the blue region of the spectrum. This could be achieved by a second APCVD process, with titanium(IV) oxide for example, or as a spin/dip coating process if an organic dye is used.

The preparation of demonstration samples in order to test the performance of vanadium(IV) oxide coated windows would be required if the commercial use of the technology is to be attempted. If successful this could then lead to full-scale production and consumer use.
## SUBSTRATE TEMPERATURE PROFILES.

Below are the temperature profiles for a glass substrate at various reactor temperatures. A glass substrate was scored into 18 sections (25 mm × 15 mm), loaded into the reactor and a thermocouple placed in each section when the reactor had reached the set temperature. All readings are in °C.

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REFERENCES

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References


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References


