

Intelligent Thermochromic Windows

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This article details the formation of vanadium dioxide thin films on glass for use as an intelligent window—a window that can change one or more of its properties in response to some external stimulus. In this case the vanadium dioxide coated glass changes its optical properties with temperature—becoming more reflective at infrared wavelengths at elevated temperature. The article covers aspects of inorganic synthesis and gives an introduction to three of the most widely used methods for forming thin films of material—chemical vapor deposition, the sol-gel process, and physical vapor deposition. It also explains the underlying physical chemistry associated with a metal-to-semiconductor phase transition and uses this to explain why thin films of vanadium dioxide and doped vanadium dioxide show such unique properties and potential. This article will help the educator to set up lectures on thin-film deposition and in applications of new materials.

Solar-Control Coatings

The use of air conditioning systems to maintain comfortable working and living environments has become more common (1). This leads to an increase in the use of electricity and a concurrent increase in carbon dioxide emissions and other atmospheric pollutants formed 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 indium-doped tin dioxide (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 (at infrared wavelengths), is prevented from escaping the building and thus reduces heating requirements (2).

A further development is the use of thermochromic coatings as intelligent window coatings (1–7). 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, Japan, the United States, and Canada, which have hot summers and cold winters.

Vanadium(IV) oxide is one example of a thermochromic (TC) material that shows promise as an intelligent window coating. A pictorial representation of how a vanadium(IV) oxide thin film will 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 blackbody 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. Minimizing the use of internal lighting also reduces building maintenance costs.

The critical temperature of vanadium(IV) oxide, 68 °C, is too high to maintain a comfortable temperature within a building (18–25 °C). Additives can influence the critical temperature of vanadium(IV) oxide (9), 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 vapor deposition methods (10) and sol-gel spin or dip coating (11). A tungsten loading of only 2 atom percent is required to reduce the thermochromic transition temperature of vanadium(IV) oxide thin films to room temperature.

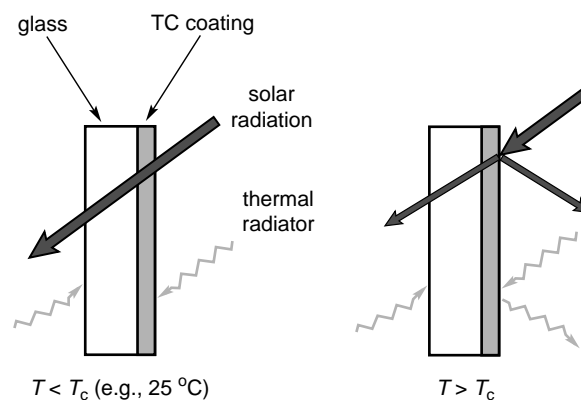


Figure 1. Schematic demonstration of the application of thermochromic materials to advanced window glazing (8).

One distinct problem reported for vanadium(IV) oxide thin films for commercial glazing applications is the low luminous transmittance of the glazing film (10–13). This results in less visible light being transmitted by the window and the subsequent necessity for increased lighting to be used in buildings that have 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 (4) attempted fluorine doping into the vanadium(IV) oxide lattice to form VO_xF_y thin films by rf sputtering. This had the important property of reducing the thermochromic transition temperature along with increasing the transmittance. Burkhardt et al. (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.

Lee et al. (12), investigated silicon(IV)-oxide overlayers that greatly improved the transmittance below and above the thermochromic transition temperature without affecting the temperature at which the transition occurred. A multifunctional window coating was prepared by Jin et al. (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. It was proposed that the composite films would have multifunctional properties as titanium(IV) oxide is a well characterized photocatalyst (14) that is used in self-cleaning window coatings (15, 16).

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 as it is made during the manufacturing process in the float-glass furnace (17). Physical vapor deposition (PVD) 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 offline processes. The ideal process for applying thin films of material to glass substrates is atmospheric pressure chemical vapor deposition (APCVD) that has the advantage of not requiring a reduced pressure environment and has the high growth rates necessary for a high throughput process.

Structure and Properties of Vanadium(IV) Oxide

Since Morin (18) investigated the thermo-conductive properties of several transition-metal oxides in the late 1950s, 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 owing to the changes in conductive properties of the materials, but other properties of these materials soon became apparent and the transition has since been relabeled a metal-to-semiconductor transition (MST). Optical properties also displayed discontinuous behavior with large decreases in transmittance and increases in reflectance on passing through the transition temperature (19, 20).

The most promising of the transition-metal oxides investigated by Morin for technological applications is vanadium(IV) oxide. This material has a MST 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 that corresponds to a structural phase transformation from monoclinic to tetragonal (Figure 2, ref 21). The low temperature, monoclinic phase has unit cell parameters $a = 5.7529 \text{ \AA}$, $b = 4.5263 \text{ \AA}$, $c = 5.3825 \text{ \AA}$, and $\beta = 122.6020^\circ$. The structure involves $\text{V}^{4+}\text{--V}^{4+}$ pairing with alternate shorter (0.265 nm) and longer (0.312 nm) $\text{V}^{4+}\text{--V}^{4+}$ distances along the monoclinic a axis. The high temperature phase has a tetragonal rutile type structure, cell parameters $a = 4.5540 \text{ \AA}$ and $c = 2.8557 \text{ \AA}$, with equidistant vanadium atoms (0.288 nm) in chains of edge sharing $[\text{VO}_6]$ 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 $\text{V}^{4+}\text{--V}^{4+}$ pairs to form a tetragonal phase allowing metallic conductivity (21). Representations of the two phases of vanadium(IV) oxide are shown in Fig-

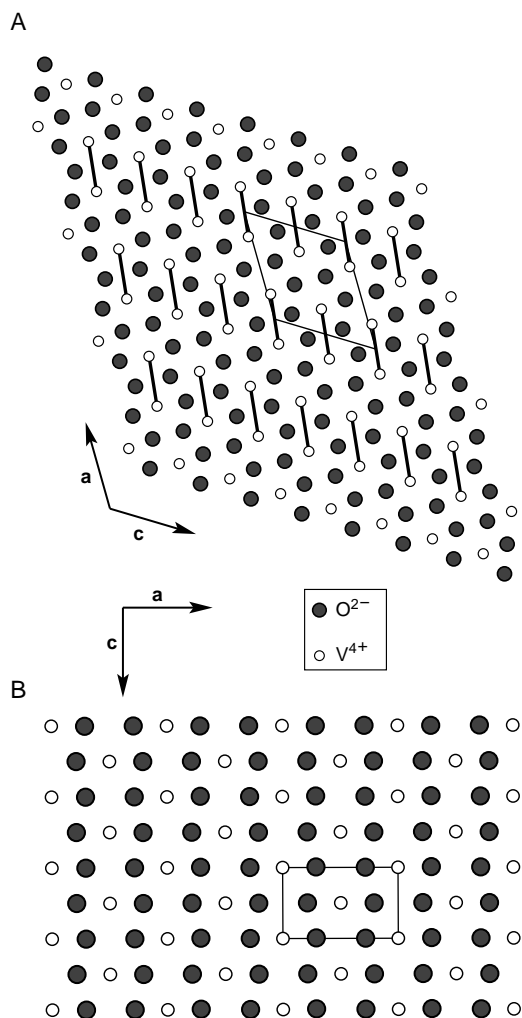


Figure 2. Representations of the structures of (A) monoclinic VO_2 , with V–V pairs indicated, and (B) tetragonal VO_2 , viewed along the b -axis of the unit cell.

ure 2 (cell parameters are taken from Rogers ref 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.

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 led to vanadium(IV) oxide being investigated, among other uses, as a potential data storage media (1, 3), an optical switch (22), and as an infrared modulator for missile guidance systems (5). It is as an intelligent window coating that vanadium(IV) oxide may find its most beneficial application.

Nature of the MST in Vanadium(IV) Oxide

Numerous theoretical studies have been undertaken to understand the details of the MST in transition-metal oxides and vanadium(IV) oxide in particular (23–28). Despite these studies, the MST is still not understood fully. The most useful theoretical discussion, from a chemist's point of view, to explain the MST of vanadium(IV) oxide is that of Goodenough (24), 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_c due to the antiferroelectric distortion and T_c' 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_c 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 article by Eyert (29) 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 behavior. 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 transition cannot be instantaneously transferred between the material and the surroundings.

Doping of Vanadium(IV) Oxide

Effect of Doping in Vanadium(IV) Oxide

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

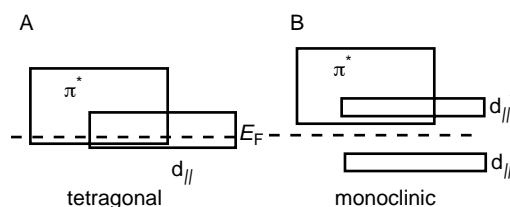


Figure 3. Band structure scheme for (A) tetragonal and (B) monoclinic VO_2 at the Fermi level (E_F) (adapted from ref 29). $d_{||}$ orbitals are due to V–V pairs resulting from overlap of $d_{x^2-y^2}$ atomic orbitals.

It was observed that high valent metal ions, for example, W^{6+} and Nb^{5+} , when substitutionally doped into vanadium(IV) oxide, decrease the MST temperature of vanadium(IV) oxide considerably, as low as room temperature with ~2 atom percent W^{6+} . Low valent ions, for example, Al^{3+} and Cr^{3+} , were shown to increase the MST temperature. MacChesney and Guggenheim (9) made the observation that dopants with an ionic radius smaller than V^{4+} , or that created V^{5+} defects that were smaller than V^{4+} , increased the MST temperature, while dopants with a larger ionic radius than V^{4+} caused a decrease in the MST temperature.

A more involved discussion was given by Goodenough (24, 30), who builds on the X-ray diffraction observations that a second semiconducting 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 semiconducting 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 (24).

Cations that cannot contribute to homopolar bonds, but can participate through p bonding—for example— Ti^{4+} d^0 , 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 stabilization of the low-temperature phase by introducing p^* electrons into the antiferroelectric state. This then reduces the antiferroelectric transition temperature, T_c . The additional electrons are often localized as discrete V^{3+} ions.

Low valent cations, for example, Al^{3+} , introduced into the vanadium(IV) oxide lattice stabilize 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 owing to having a high preference for octahedral coordination.

The work of Goodenough has been further confirmed by Tang et al. (31) who investigated the oxidation states of vanadium and tungsten in $W_{0.05}V_{0.95}O_2$ and $W_{0.08}V_{0.92}O_2$ 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.

Tungsten Doping

Of the dopants investigated so far in single crystals and PVD or sol-gel prepared thin films, tungsten (32–37) has been found to reduce the transition temperature of vanadium(IV) oxide by the greatest extent and as such is the dopant that been the focus of the most research. For all methods of preparation, vanadium(IV) oxide films containing ~2 atom percent tungsten have been shown to have a thermochromic transition temperature of about 25 °C, the ideal transition temperature for intelligent window coatings.

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 MST temperature of vanadium(IV) oxide. As discussed above, 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 (36–39). Other metal ions have also been doped into the vanadium(IV) oxide lattice by sol-gel methods, including gold (40), molybdenum (41), niobium (42), and aluminium (36). 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 (43).

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 MST temperature, namely tungsten (10, 33, 34), and molybdenum (44–45). Iron doping of vanadium(IV) oxide by PVD showed a minimum thermochromic transition temperature with 1.4 atom percent Fe at 59 °C on the heating cycle (46).

Vanadium(IV) oxide film doped with 1.2 atom percent fluorine (fluorine replacing oxygen atoms) has been shown to reduce T_c to 20 °C, but also causes the hysteresis width of the thermochromic transition to broaden appreciably, making fluorine doping unsuitable for window coating (10). 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 (47).

Film Stresses and Their Effect on the Thermochromic Transition of Vanadium(IV) Oxide

Pure, bulk crystalline vanadium(IV) oxide displays a MST at 68 °C. Most thin films of vanadium dioxide also display the transition at the same temperature. However there have been reports in the literature where very thin films (ca. 200 nm) of pure vanadium(IV) oxide have shown transition temperatures lower than 68 °C (41, 48, 49). Maruyama et al. (48) link the variations in the thermochromic transition temperature to the thickness of the thin film, but do not suggest a mechanism for the effect. Case (49), however, investi-

gates the effects of mismatches in substrate-film expansion coefficients that cause extrinsic stresses in the film crystallites. He also uses low-energy ion bombardment to cause intrinsic stresses in the thin film. Both effects are shown to decrease the temperature at which the MST occurs. Rakotoniaina et al. (50) also discuss 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 thermochromic transition temperature.

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 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 (9). Guzman et al. (51) 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 vapor deposition (PVD), and chemical vapor deposition (CVD). Of these CVD has attracted less interest owing 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. CVD 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.

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 multistage, offline processes. For the formation of vanadium(IV) oxide this involves partially hydrolyzing the initial coating and then heating it in a reducing atmosphere to form crystalline vanadium(IV) oxide. 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 tri(*iso*-propoxide), followed by vanadyl tri(*tert*-amyloxide). 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. (37) that used metallic vanadium dissolved

in 30% H_2O_2 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 (37, 43).

PVD Method

The second general method discussed here involves PVD techniques (52). 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 quantity of material removed from the target and the quantity 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 degree of doping can be easily controlled by the relative sizes of the targets.

CVD Method

The final method used to prepare thin films of VO_2 is CVD. In particular atmospheric pressure chemical vapor deposition (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 to our knowledge and prior to our work not been reported in the literature. Pure vanadium(IV) oxide films have been produced by CVD onto glass substrates (42). Vanadyl tri(*iso*-propoxide) or vanadyl tri(*iso*-butoxide) (53) 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 VCl_4 or VOCl_3 and an oxygen source such as water or ethanol (54) or with carbon dioxide (55). 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, $\text{V}(\text{acac})_3$, by an APCVD method followed by slow post-deposition cooling (48), and from vanadium(IV) acetylacetonate, $\text{V}(\text{acac})_4$, by a pyrolysis method in a controlled atmosphere (56). Vanadyl acetylacetonate, $\text{VO}(\text{acac})_2$, has been used to prepare the

metastable $\text{VO}_2(\text{B})$, which can be converted to the tetragonal phase by annealing in argon at 500 °C (57–58). Vanadyl precursors have also been used in a CVD method to prepare various vanadium oxide thin films including vanadium(IV) oxide (59). 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 process is required that utilizes inexpensive, readily available precursors that will produce vanadium(IV) oxide directly without the need for a reduction step.

Comparison of the Different Production Methods

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 owing 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 offline processes can often 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 (17).

APCVD Method

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, ref 60):

- Transport of the reactive species to the reaction site
- Gas-phase reaction
- Adsorption onto the substrate surface
- Nucleation on the substrate surface
- Reaction and desorption of byproducts
- 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 by hot, inert carrier gas. The substrate

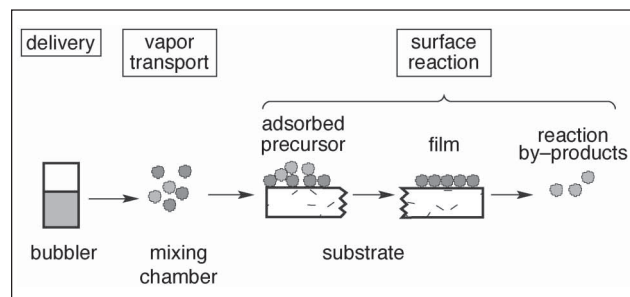


Figure 4. Pictorial representation of the atmospheric pressure chemical vapor deposition process.

temperature also needs to be relatively high to initiate the deposition.

In the reaction chamber two types of reactions may occur: homogeneous reactions occurring entirely in the vapor phase and heterogeneous reactions occurring at the vapor–solid surface interface (61). In cold wall reactors the homogeneous reactions and heterogeneous reactions at the reactor walls are suppressed owing to the lower heat input to the system. Vapor–substrate reactions are therefore more important (61). Little is known about these types of reactions owing 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.

Two precursor systems to prepare thin films of tungsten-doped vanadium(IV) oxide (62–64) have been used. First, tungsten(VI) ethoxide was introduced into the APCVD of vanadium(IV) chloride and water. This gave vanadium(IV) oxide thin films containing between 0.3 and 1.2 atom percent tungsten and with thermochromic transition temperatures of 58 °C for a 0.3 atom percent tungsten-doped film to as low as 42 °C for a 1.2 atom percent 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 vapor pressure and transport properties prevented tungsten contents of much greater than 1.2 atom percent from being introduced into the vanadium(IV) oxide lattice.

The thermochromic properties of these films did show promise as intelligent window coatings with reduced transition temperatures and the typical change in optical properties associated with undoped vanadium(IV) oxide (Figure 5). 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) cat-

ions, 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 that would have degraded the thermochromic properties of the thin films.

The second tungsten precursor investigated was tungsten(VI) chloride (63, 64), which was introduced into the APCVD of vanadium(V) oxytrichloride and water. This system was much more successful than the tungsten(VI) ethoxide system, as the higher vapor pressure and transport properties of tungsten(VI) chloride enabled a greater quantity of tungsten to be introduced into the vanadium(IV) oxide lattice. Tungsten contents as high as 3 atom percent were observed that gave thermochromic transition temperatures as low as 5 °C. A tungsten content of 1.9 atom percent gave a thermochromic transition temperature of 29 °C, which is around the ideal for intelligent window coatings. It was noted that the decrease in transition temperature was linear with tungsten atom percent incorporation (Figure 6). 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 thin films, suggesting a reduction from the tungsten(VI) chloride precursor during the CVD process.

Summary

Intelligent thermochromic glass can be made that can switch at the desired temperatures, 25–30 °C. The precise switching temperature can be chosen by the level of tungsten doping. These coatings can be made by a process compatible with commercial glass manufacture—APCVD. The challenges to be overcome in producing a commercial product include: color—the films are yellow brown; scaleup—will

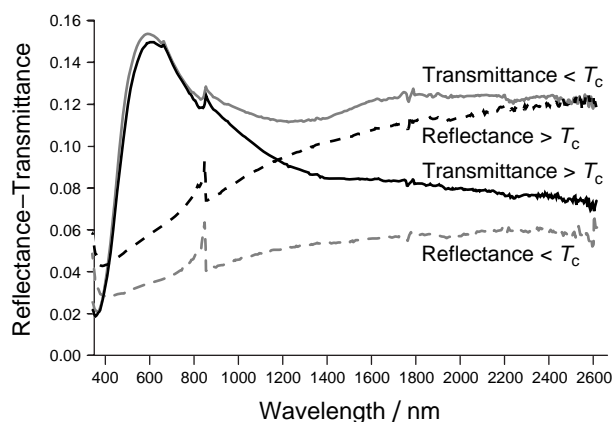


Figure 5. Reflectance–transmittance spectra for a 0.6 atom percent W doped VO_2 thin film below and above the thermochromic transition temperature. Discontinuities are due to lamp and filter changes in instrument.

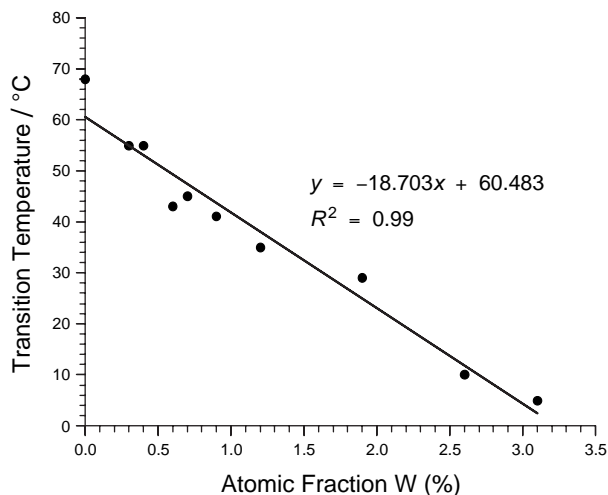


Figure 6. Change in observed thermochromic switching temperature of VO_2 with W atom percent.

the precursor chemistry work on an industrial scale; weathering—will the coating survive environmental conditions; thermal cycling—will the coating survive repeated temperature cycles. Most if not all of these issues could be resolved—color could be improved by doping or by use of refractive index matched over or under layers; weathering—not an issue if used as an internal pane of a double glazed unit; thermal cycling—CVD films are generally robust and to date have shown no deterioration in film properties after hundreds of thermal cycles.

There is no doubt that a large market will be available for a commercial thermochromic glass. This will include household, office, and factory window applications as well as automotive applications and even applications for space exploration—a material that can switch its infrared reflection properties with temperature is very desirable in order to keep spacecraft components at the correct temperature. It also has potential in fire-retardant clothing.

Acknowledgments

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